I

TID-5221

POLONIUM

Editor

HARVEY V. MOYER
Professor of Chemistry, The Ohio State University

Associate Editors

LLOYD B. GNAGEY
Mound Laboratory, Monsanto Chemical Company

ADRIAN J. ROGERS
Mound Laboratory, Monsanto Chemical Company

Oak Ridge, Tennessee
United States Atomic Energy Commission
Technical Information Service Extension
July 1956

s document is
RELEASABLE
Williams
fficial
2007

DISCLAIMER

III

POLONIUM

Printed in U.S.A., price $1.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AEC, Oak Ridge, Tenn.

CONTRIBUTING AUTHORS

David S. Anthony
J. E. Campbell
George W. Charles
R. N. Cowden
G. C. Cox
R. K. Davis
R. R. Deem
R. W. Endebrock
P. M. Engle
Lloyd B. Gnagey
James M. Goode
P. M. Hamilton
Warren L. Hood
F. M. Huddleston
E. F. Joy
F. C. Mead, Jr.
Harvey V. Moyer
G. D. Nelson
John L. Richmond
Adrian J. Rogers
C. E. Shoemaker
Edward Spoerl
John S. Stanton
J. W. Wright
R. E. Zipf

ACKNOWLEDGMENTS

The compilation of a reference text of the nature of this volume is the culmination of the coordinated effort of many people whose names do not appear either as authors or as cited references. The editors gratefully acknowledge the assistance given by all such personnel. The editors also wish to express their appreciation for the generous cooperation extended by the United States Atomic Energy Commission.

This book was prepared under the general supervision of J. W. Heyd, with the exception of some of the preliminary phases which were under the direction of E. Orban.

Checking of this text for technical accuracy was done by J. E. Bradley, J. W. Heyd, K. C. Jordan, M. McEwen, and D. L. Scott.

Particular credit is due M. McEwen for an extensive summary and bibliography on polonium which he compiled in 1948. This compilation was a constantly used reference source and essentially furnished the outline for much of Chap. 7.

The photography is the work of F. J. Gorman and T. H. Martin. Many of the drawings were prepared especially for this volume; these were the work of Betty Halley and Helen Hudson. H. E. Sergent was helpful in giving technical assistance pertaining to the preparation of photographs and drawings.

Special editorial assistance was given by W. H. Waldo. Special writing assistance was given by G. W. Wright. The editors are especially indebted to Geneva Miller who typed most of the final copy through many editorial changes. Thanks are also due Virginia Gerrard, Margaret laze, Helen Pride, and Jean Whitehead for their typing assistance.

Finally, the editors wish to thank all of the Mound Laboratory pernnel who answered the many questions which arose concerning vari aspects of the polonium program.

Harvey V. Moyer
Lloyd B. Gnagey
Adrian J. Rogers

MOUND LABORATORY FOREWORD

Shortly after the inception of the atomic energy program it became apparent that more chemistry was involved in the program than had originally been anticipated. Members of the Manhattan Engineer District discussed their problems with Dr. Charles Allen Thomas, then Director of the Central Research Department, Monsanto Chemical Co., who was serving on the National Defense Research Committee as coordinator of chemical research with the Manhattan Engineer District. The Monsanto Chemical Co. then undertook the task of solving, at its Dayton facility, some of the chemical problems.

Dr. Thomas was the first Project Director with Dr. Carroll A. Hochwalt as Assistant Project Director. When Dr. Thomas was appointed Director of Clinton Laboratories, Dr. Hochwalt became Project Director. Dr. James H. Lum and Dr. N. N. T. Samaras were the first Monsanto scientists cleared for the project. Although Dr. Samaras was soon assigned to other duties in the Company, he returned as Project Director in 1951 and still continues in this position. Dr. Lum was the first Laboratory Director and was succeeded by Dr. W. C. Fernelius. After Dr. Fernelius left the Dayton Project, Dr. Malcolm M. Haring was named Laboratory Director and served in that position until his death in January 1952. Dr. Joseph J. Burbage, one of the first persons recruited by Monsanto for work on the atomic energy project, succeeded Dr. Haring as Director of Mound Laboratory and served in that capacity until he was appointed to another position in the company in March 1955. The present administrative head of Mound Laboratory is Edward C. McCarthy.

Monsanto began preliminary organization and personnel recruiting at the Company's Central Research Department, a permanent installation on Nicholas Road in Dayton, Ohio. When Central Research activities began to expand to other temporary sites in Dayton during World War II, the original Nicholas Road location was designated as Unit I. Spectrographic and X-ray work for the project remained at this location until Mound Laboratory was completed in 1949.

As a result of their expanding activities, Monsanto leased a property at 1601 West First Street in Dayton from the Dayton Board of Education. The original building on the site had been constructed in 1879 to house Bonebrake Theological Seminary; it was later used as a normal school and then as a warehouse by the Dayton Board of Education. Monsanto had to undertake considerable repair and renovation to fit the building for service as a laboratory, and other laboratory and service facilities were added until the site finally contained 20 buildings. It was referred to as Unit III of Monsanto's Central Research Department (Unit II was another government project, not related to atomic energy), and it was used, in part, for research into the extraction and purification of polonium for the preparation of neutron sources and alpha sources and the treatment of residues from these processes. The temporary structures were eventually dismantled, and the original building was returned to the Board of Education in 1950 after intensive decontamination operations had been completed.

Meanwhile the Corps of Engineers had rented Runnymede Playhouse for use by the project, and Monsanto took possession of this site as Unit IV of its Dayton operations. This building was located on Runnymede Road in Oakwood, a fine residential suburb of Dayton, and had originally been constructed by a wealthy family for recreational uses. It included such unique features as a corrugated glass roof, several greenhouses, an inside tennis court, a stage, and squash courts; and had several lounges, a boiler room, and an outside swimming pool. This site was utilized by Monsanto for part of its atomic energy research and development program until Mound Laboratory was completed in 1949. By that time the basic structure had become so contaminated with radioactivity that decontamination was impossible; therefore the building was completely demolished, and the foundations were covered with dirt and sod. Demolition began in February 1950 and was completed in the early summer, after which the site was returned to the Corps of Engineers for disposition.

By late 1945 the Manhattan Engineer District reached the conclusion that the research organization operated by Monsanto at Dayton should be made a permanent facility. Early in 1946 a search was made for a suitable location. The site selected was a 178-acre plot about 12 miles south of Dayton on the edge of the town of Miamisburg, Ohio. The land was adjacent to a state park containing an aboriginal Indian mound from which Mound Laboratory eventually took its name. In July 1946 Monsanto was authorized to proceed with the design of the plant, then referred to as Unit V. Monsanto engaged the firm of Giffels and Vallet of Detroit to perform design services, and the plant was built by the Maxon Construction Co., Dayton, Ohio, under a prime contract with the Manhattan Engineer District. Buildings were occupied as they were completed, the first in May 1948. Processing of polonium for the production of neutron sources and alpha sources began in February 1949.

At the same time that Monsanto was authorized to proceed with the design and construction of a permanent plant, Col. Robert J. Kasper was assigned by the Manhattan Engineer District as Area Engineer for the project. He remained as Area Manager when control of the atomic energy program passed to the United States Atomic Energy Commission in January 1947. Mr. Kenneth A. Dunbar was appointed Manager of the Dayton Area Office in April 1947, and he was succeeded in February 1950 by Mr. Fred H. Belcher. Dr. John H. Roberson became Area Manager in May 1952.

CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CONTENTS

CHAPTER 8

CHAPTER 9

CHAPTER 10

CHAPTER 11

CHAPTER 12

CHAPTER 13

TID-5221

Chapter 1

SURVEY OF EARLY OPERATIONS

By Harvey V. Moyer

1. INTRODUCTION

Polonium had not been isolated in pure form in weighable amounts prior to 1944. It was discovered in 1898 by Pierre and Marie Curie,[1] who observed a higher radioactivity in pitchblende than was expected from its content of uranium and thorium. They separated the polonium from a ton of pitchblende by following its radioactivity in the concentration process. They found it consistently in the bismuth-containing fractions and consequently suspected its chemical similarity to bismuth. A pure end product was not obtained by their method of preparation, but in their first attempt they succeeded in obtaining a sample of polonium which was 400 times as active as uranium. Pure polonium is approximately 6.5×10^9 times more active than uranium. They named the element "polonium" in honor of Poland, the native land of Marie Curie. One of the largest preparations of polonium in early times was made by Marie Curie and Debierne,[2] who started with several tons of the residue from the sulfuric acid extraction of uranium ore. Their final preparation weighed about 2 mg and probably contained approximately 0.1 mg of polonium.

Polonium was not recognized with certainty as a new element for 7 or 8 years after its discovery. Marckwald, who made valuable contributions to the procedure for isolating polonium, at first doubted the identity of his preparations with those of the Curies. He was impressed by its similarity to tellurium and suggested the name "radiotellurium."[3–5] He separated it from bismuth by reduction with stannous chloride and also discovered that tellurium could be precipitated by reduction with hydrazine, which under certain conditions did not reduce polonium to the metallic state. He observed that polonium deposited spontaneously on silver and on metallic bismuth.[6]

Recognition of polonium as a new element became general about 1905, after Hofmann, Gonder, and Wölfl[7] had reported the results of their experiments on the repeated electrolysis of lead solutions obtained from pitchblende and after the half-life measurements by Rutherford[8] had proved that radiotellurium and polonium were identical.

Those radioisotopes which emit alpha particles have been of considerable interest to the Dayton Project and to Mound Laboratory. A significant portion of the research activities at these installations has been directed toward acquiring information on this type of radioactive-particle emitter. The preparation of neutron sources and alpha sources has constituted a major interest at these sites, and as a result of investigations for improving source-preparation processes, a considerable wealth of "by-product" information on the physical, nuclear, chemical, and biological properties of alpha emitters has been accumulated. Polonium, which was one of the radioisotopes investigated, is almost a unique alpha emitter in that: (1) it is relatively free of other types of radiations; (2) it decays directly to a stable isotope; (3) it is found in nature or it can be artificially produced; (4) it has a decay half life which gives excellent specific-activity characteristics for research purposes as well as for commercial purposes; (5) it has a high relative volatility which assures ease in partial purification of the element by volatilization as well as permitting ease in the preparation-by-volatilization of neutron sources and alpha sources; (6) it may be purified by any one of several methods (either small or large scale operations are practicable); and (7) it emits a sufficiently energetic alpha particle to satisfy the requirements of most users of the element.

2. SOURCES OF POLONIUM

The largest concentration of polonium prior to the irradiation of bismuth in a nuclear reactor came about incidentally in the commercial processing of uranium ores for the production of radium. A mixture of active and inactive lead, known officially as "radiolead,"[9] is precipitated as lead sulfate in the radium-refining process. Polonium is formed spontaneously as a result of the decay of radioactive lead (RaD^{210}):

$$\begin{tikzcd}
 & & \begin{array}{c}{}_{84}\text{RaF}^{210}\\ \text{(Po)}\end{array} \arrow[dr, "\alpha"] & \\
\begin{array}{c}{}_{82}\text{RaD}^{210}\\ \text{(Pb)}\end{array} \arrow[r, "\beta^-"] & \begin{array}{c}{}_{83}\text{RaE}^{210}\\ \text{(Bi)}\end{array} \arrow[ur, "\beta^-"] \arrow[dr, "\alpha"'] & & \begin{array}{c}{}_{82}\text{RaG}^{206} \text{ (stable end product)}\\ \text{(Pb)}\end{array} \\
 & & \begin{array}{c}{}_{81}\text{Tl}^{206}\\ (\sim 10^{-5}\%)\end{array} \arrow[ur, "\beta^-"'] &
\end{tikzcd}$$

The equilibrium ratio of uranium to polonium is 1.19×10^{10}. Consequently pitchblende, which contains from 25 to 55 per cent uranium, may contain a maximum of 0.02 to 0.04 mg of polonium per ton. Paneth and Hevesy[9] state that radiolead precipitated from uranium ores might contain as much as 2 mg of polonium per ton. However, this relatively high content of polonium was not found by Fernelius and Larsen,[10] who assayed numerous samples of radioactive lead dioxide from the Port Hope radium refinery in 1943. They reported that 6 tons of lead dioxide was available which contained 0.2 to 0.3 mg of polonium per ton. It was estimated that if the Belgian Congo uranium ore were processed, the polonium content in the lead dioxide from this source might reach 0.6 mg/ton. Prior to 1944, a small quantity of polonium was obtained from spent radon tubes. These tubes, filled with radon, were used for therapeutic irradiations. Minute quantities of polonium in fairly pure form were obtained from these tubes by a simple procedure for separating it from the two isotopes of lead (RaD and RaG). The quantity of polonium, estimated as available from spent radon tubes in 1943, was entirely too small for the production of weighable amounts of the element.

3. THE DILLON PATENTS[11-14]

Few attempts have been made to use polonium industrially; however, a number of U. S. and Canadian patents were issued to John H. Dillon and assigned to The Firestone Tire & Rubber Company, Akron, Ohio. These patents describe a process for obtaining polonium for use in the manufacture of electrodes for spark plugs. Claims are made that the procedure is commercially applicable to the production of polonium from lead residues obtained in the refining of radium. Several variations in procedure are described, but the most successful method according to Dillon and Street[15] started with radioactive lead dioxide. This was converted to lead chloride by treating it with concentrated hydrochloric acid:

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$

The lead chloride was washed until it was only slightly acid, and then it was added to a solution of 0.03N hydrochloric acid which was heated to boiling during the plating process. The polonium deposited spontaneously in 12 to 14 hr on etched nickel plates which were suspended in the boiling acid solution. After the removal of the polonium, the lead chloride which precipitated on cooling was stored in earthenware crocks for a period of 6 to 12 months. At the end of the aging period the plating operation was repeated to recover the polonium which had formed by the further decay of radium-D. In these operations the polonium was not removed from the nickel plates; these were dissolved directly in the alloy melts for the production of electrodes for spark plugs. Dillon claimed to separate 15 to 20 μg of polonium from a 50-lb batch of lead chloride at each “milking.” This yield of polonium is approximately 3.0 curies per ton of lead dioxide. (One curie of polonium is equivalent to 0.222473 mg.[16])

4. PREPARATION OF POLONIUM BY THE MONSANTO CHEMICAL CO.

4.1 *General.* A survey[10] of the possible sources of polonium was made in 1943, and it was agreed that irradiated bismuth appeared to be the most promising ultimate source of polonium. However, since the irradiation process had not been developed to the production state, it seemed desirable in the meantime to use some natural source of polonium. It was decided, therefore, to undertake the separation of polonium from the radioactive lead residues from the Port Hope radium refinery. The production schedule at Port Hope called for 30 curies of radium per month; hence this appeared to be an excellent potential source of polonium.

The first shipment of approximately 3½ tons of lead dioxide was received in Dayton from Port Hope in November 1943. Altogether, nearly 37 tons of lead dioxide were received and processed up to May 1945, when operations with the lead process were discontinued. The total quantity of polonium obtained from this source amounted to approximately 40 curies.

Three possible methods were investigated for the production of polonium from radioactive lead residues: (1) the lead chloride (Dillon) process, (2) a dry thermal volatilization method, and (3) a wet chemical method. The last process is discussed in detail in Chap. 6.

4.2 *Lead Chloride Process.* The Dillon process appeared from the patent literature to be a workable method which could be put into immediate operation. After preliminary laboratory experiments indicated that the process was workable, operations on a comparatively small scale were undertaken at the Monsanto Chemical Co. plant at Monsanto, Ill., early in 1944. By Mar. 1, 1944, 3 tons of radioactive lead had been processed, and approximately 2.5 curies of polonium had been deposited on nickel and copper plates. This represented an estimated efficiency[17] of about 80 per cent in the removal of the polonium from the lead dioxide.

The plating of the polonium on copper and nickel strips by no means completed the process of isolating the element because at this stage the 0.5 mg of polonium was spread over 461 metal plates with a total surface area of approximately 1700 sq ft. Attempts to concentrate and collect the polonium from the metal surfaces by distillation in a large quartz still were only partially successful, and because, by March 1944, other production processes had proved more promising, the lead chloride project was abandoned.

4.3 *Kiln Process.*[18] The volatility of polonium was recognized by the early workers.[1] Hofmann, Gonder, and Wölfl[7] observed that the alpha activity could be removed from the electrodes by heating to bright red heat. Rutherford[19] reported that the alpha and beta activities from radioactive lead could be separated by heating the active deposits on platinum foils to 1000°C. Russell and Chadwick[20] described a procedure for distilling polonium from metal foils and collecting the volatilized element on cooled aluminum strips. It appeared probable, therefore, that polonium might be separated from lead dioxide by direct heating. Preliminary laboratory experiments indicated that the activity could be removed from lead dioxide by heating to 600 to 700°C in a stream of carbon dioxide. Two small stainless-steel kilns were built[21] and tested. The first was an agitator type with a capacity of 3 to 8 lb, and the second was a rotary type with a capacity of about 15 lb. The latter was built with dimensions proportional to a proposed production model. In the first runs with the agitator-type kiln, lead dioxide was used, but the charge sintered at 700°C with the result that in one run the slag had to be chiseled out of the kiln. Since the formation of slag prevented stirring the charge and since it was discovered also that the volatilization of polonium was incomplete at 700°C, it was decided to use lead orthophosphate which was less fusible than lead dioxide. All subsequent runs in the kilns were made with lead orthophosphate which was prepared by treating lead dioxide directly with phosphoric acid. Pilot-plant runs in the small kiln indicated that it was necessary to heat the lead phosphate in a current of carbon dioxide at least 4 hr at 750°C in order to remove the activity. Various types of condensers for collecting the polonium were tested. The most successful was a water-cooled brass finger containing a Pyrex glass-wool filter. However, results were inconsistent, caused, in part, by the difficulties in screening out inactive dust particles and in preventing the fine dust from carrying the active material through the filters. Several runs were made with the second kiln, which operated quite well mechanically, but the volatilization and collection data were not encouraging. Dusting also was greater than anticipated with the result that machinery and personnel were grossly contaminated. In the meantime a chemical process had been developed which appeared sufficiently promising to justify discontinuing the work with the kilns.

4.4 *Chemical Process.* The chemical treatment of the Port Hope lead dioxide proved to be the most successful method of obtaining polonium prior to the development of the irradiated-bismuth process. The first step in the procedure[22] was the treatment of the lead dioxide with concentrated nitric acid and 27 per cent hydrogen peroxide to convert the lead dioxide to lead nitrate:

$$PbO_2 + 2HNO_3 + H_2O_2 \rightarrow Pb(NO_3)_2 + O_2 + 2H_2O$$

Prior to filtration of the insoluble portion of the ore, lead carbonate was added to reduce the acidity to approximately pH 4.0. This addition caused the precipitation of a number of undesirable elements, including iron and aluminum. The insoluble siliceous residue which was separated by filtration was a complex mixture which carried with it the polonium which had grown in the lead dioxide prior to treatment. The recovery of polonium from radioactive lead residues involved operations in two directions: (1) recovering the polonium initially present in the lead dioxide and (2) the periodic milking of the solution of lead nitrate obtained by dissolving the lead dioxide.

The actual quantity of polonium produced by the lead process was small (approximately 40 curies). Most of this came from the extraction of the insoluble siliceous residue remaining from the dissolution of the lead dioxide. The milking of the lead nitrate solutions did not proceed beyond the pilot-plant stage, although a total of 35 tons of lead dioxide was treated to prepare the nitrate solutions.

4.5 *Bismuth Process.* The first irradiated bismuth was received from the Clinton reactor. The nuclear reactions are

$$_{83}Bi^{209} + {}_0n^1 \rightarrow {}_{83}Bi^{210}(RaE) \xrightarrow{\beta^-} {}_{84}Po^{210}$$

The bismuth from the Clinton reactor contained from 0.032 to 0.083 curie of polonium per kilogram of bismuth. Thus a ton of the first irradiated bismuth contained from 29 to 75 curies of polonium, a vast increase over the yield of 1 to 3 curies per ton from the Port Hope lead dioxide. The separation of polonium from bismuth and its purification will be discussed in detail in later chapters since this is the present source of polonium.

REFERENCES

1. P. Curie and M. Curie, Compt. rend., 127: 175-178 (1898).
2. M. Curie and A. Debierne, Compt. rend., 150: 386 (1910).
3. W. Marckwald, Ber., 35: 4239 (1902).
4. W. Marckwald, Ber., 36: 2663 (1903).
5. W. Marckwald, Ber. deut. pharm. Ges., 13: 14 (1903).
6. W. Marckwald, Ber., 38: 591 (1905).
7. K. A. Hofmann, L. Gonder, and V. Wölfl, Ann. Physik, 15(4): 620 (1904).
8. E. Rutherford, Phil. Mag., 10(6): 290-306 (1905).
9. F. Paneth and G. V. Hevesy, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa, 122: 1002 (1913).
10. E. M. Larsen and W. C. Fernelius, Possible Sources of Polonium, Information Report No. 26, MLM-46-8-65, Oct. 29, 1943.
11. U. S. Patent No. 2,254,169, Aug. 26, 1941.
12. U. S. Patent No. 2,254,170, Aug. 26, 1941.
13. Canadian Patent No. 541,302, Nov. 21, 1941.
14. Canadian Patent No. 419,186, Mar. 21, 1944.
15. J. H. Dillon and J. N. Street, J. Appl. Phys., 13: 189-198 (1942).
16. H. H. Fox, Recalculation of Fundamental Constants and Conversion Factors, Report MLM-960, Jan. 4, 1954.
17. J. J. Burbage, The Lead Chloride Process, Final Report No. 4, MLM-M-1260, Mar. 17, 1944.
18. L. R. Hill, M. L. Nielsen, and H. R. Weimer, Kiln Process, Final Report No. 27, MLM-M-1061, Aug. 31, 1945.
19. E. Rutherford, Trans. Roy. Soc. London, A204: 200 (1905).
20. A. S. Russell and J. Chadwick, Phil. Mag., 27: 115 (1914).
21. E. C. Bratt, Historical Report, Dayton Project, Report MLM-M-286, Oct. 31, 1947.
22. H. G. Kuivila, H. R. Weimer, and R. G. Yalman, Recovery of Polonium from Radioactive Lead Dioxide, Final Report No. 11, MLM-M-1024, July 1, 1945.

Chapter 2

NUCLEAR PROPERTIES OF POLONIUM

By James M. Goode

1. ISOTOPES OF POLONIUM

1.1 *Naturally Occurring Isotopes.* One or more isotopes of polonium have been known since the discovery of RaF (Po^{210}) by the Curies[1] in 1898. Six other polonium isotopes, Po^{211} (AcC′), Po^{212} (ThC′), Po^{214} (RaC′), Po^{215} (AcA), Po^{216} (ThA), and Po^{218} (RaA), became known and their properties studied as a result of their intermediate position in the natural radioactive decay systems of radium, actinium, and thorium. Po^{211} was identified by Marsden and Wilson[2] as a result of their investigation of the branching in the decay of Bi^{211} (AcC). Po^{212} was postulated by Marsden and Barratt[3] to explain the branching in thorium-C, and its existence was verified by Barratt[4] when he determined the range of the Po^{212} alpha particle. Hahn and Meitner's investigation[5] into the radioactive decay of radon directed Fajans[6,7] to the discovery of Po^{214}. Po^{215} was described by Rutherford,[8] Geiger and Marsden,[9] and Geiger.[10] Based on the investigation of Geiger and Marsden,[11] Rutherford and Geiger[12] showed the existence of Po^{216}. Rutherford[13] postulated the existence of Po^{218} as one of the decay products of radon, and Bragg and Kleeman[14] measured the range of the alpha particle from this isotope; however, Rutherford[15] attributed this alpha-range measurement to the correct isotope.

1.2 *Artificially Produced Isotopes.* Twelve other isotopes of polonium have become known recently, either as a result of the bombardment of lead and bismuth with high-energy particles or as a result of artificially produced decay chains. Po^{213} was produced as a result of the alpha decay of Em^{217}, which occurs in the decay chain of artificially produced U^{229} (see reference 16). Po^{217} is the product of the alpha decay of Em^{221} (see reference 17). The neutron-deficient polonium isotopes (Po^{200} to Po^{210}) have been produced by bombardment of bismuth and lead isotopes with high-energy deuterons and alpha particles. The production of these isotopes has been carried out by a group at the University of California Radiation Laboratory.[18–21] The neutron-deficient isotopes have been observed to decay by alpha-particle emission or by orbital-electron capture, except for Po^{203} for which no alpha particle has been observed. The neutron-rich polonium isotopes are alpha emitters in general, although some (Po^{215}, Po^{216}, and Po^{218}) have been reported to decay, to a small extent, by beta emission. The alpha-particle energies of the polonium isotopes range from 4.86 Mev for Po^{209} to 8.78 Mev for Po^{212}; the half lives range from approximately 3×10^{-7} sec to approximately 100 years for Po^{212} and Po^{209}, respectively. A presentation of some of the nuclear properties (origin, half life, mode of decay, radiation, and radiation energy) of the polonium isotopes can be found in the Table of Isotopes, compiled by Hollander, Perlman, and Seaborg.[22]

2. HALF LIFE OF Po^{210}

2.1 *General.* The half life of Po^{210} has been studied frequently since its discovery by the Curies.[1] The half life has been reported to be within the limits of 129 to 148 days,[23] with most of the values close to the value of 140 days reported by M. Curie.[24] The values reported prior to 1946, however, were obtained with minute samples of uncertain purity which greatly handicapped the attainment of a high degree of precision. Subsequent to 1946, four determinations of the half life of polonium were made; three measurements (using relatively large quantities of polonium) were made by calorimetric methods, and one measurement used counting techniques.

2.2 *Half Life by Counting.* A half-life determination based on a counting technique was made by Curtis[25] at Mound Laboratory. The sample was prepared by deposition of approximately 0.5 mc of purified Po^{210} onto a glass slide from a nitric acid solution. The sample was covered with mica weighing 0.92 mg/sq cm, with an additional cover of thin rubber hydrochloride. The sample was counted over a period of 328 days in a low-geometry attachment (Chap. 9, Sec. 3.1) for a methane-flow proportional alpha counter. The sample was kept in the counting chamber during the experiment to avoid any possible change in geometry. Tests made by changing the air pressure in the evacuated counting chamber showed that no counts were lost by sample absorption.

Eighty-one measurements of the counting rate were made, each measurement consisting of two or more separate counts totaling at least 5×10^5 counts. A small background correction was applied to account for the increase of background counts during the course of the experiment. The observed counting rate varied from approximately 46,000 to 9000 counts/min.

The half life was determined by a least-squares best fit of the data. The half life of polonium, found by counting, was 138.374 ± 0.032 days.

2.3 *Half Life by Calorimetric Methods.* Beamer and Easton[26] have reported a value of 138.3 days ± 0.1 per cent for the half life of Po^{210}. Their value was obtained by measuring the rate of decrease of heat released by the polonium as a function of time. Two samples were used, one containing 10.93 curies of polonium and the other containing 14.35 curies.[27] The measurements were taken over periods of 97 and 73 days, and half lives of 138.32 and 138.26 days were obtained for the two samples. The apparatus used to measure the heat released by the polonium was a steady-state twin-bridge calorimeter similar to that developed by Coulter[28] at the Dayton Project in 1944.

Another recent determination of the half life was made by Ginnings and coworkers[29] of the National Bureau of Standards; they obtained a value of 138.39 days ± 0.1 per cent. This value was calculated from 21 measurements of the heat released by a polonium sample, taken at three intervals over a period of time. A modified Bunsen ice calorimeter developed at the National Bureau of Standards was used to measure the heat released. This was determined by measuring the volume change of the ice-water mixture as the ice melted. The volume change was determined by weighing the amount of mercury forced into the calorimeter to replace the volume lost as the ice melted. The calorimeter was calibrated in terms of the weight of mercury used when an electrical heater was placed inside the calorimeter and used as a source of heat. This calibration was considered accurate to within about 0.01 per cent. Two sources of heat loss were considered in computing the reliability of the calorimetric values. A small correction was made to account for the heat loss of the calorimeter to its surroundings. Another small correction was made to account for the rise in temperature of the inner portion of the calorimeter and the sample as the ice melted, decreasing the thermal contact with the ice. The sample fitted snugly on the inside of a central tube, and ice was frozen to copper fins fitted to the outside of this tube. The central unit was fitted with a series of Dewar flasks to reduce heat losses.

The half life of Po^{210} has also been measured by Eichelberger and coworkers[30] of Mound Laboratory using calorimeters of the Rutherford and Robinson[31] steady-state twin-bridge type developed at the Dayton Project and Mound Laboratory. They found a value of 138.4005 ± 0.0051 days for the half life. This value was the grand mean result obtained from six series of measurements of five different samples using four different calorimeters. (A detailed discussion of the calorimeters used may be found in Chap. 10.)

The calorimeters used for these measurements were immersed in a temperature-regulated water bath maintained to within 0.001°C. The bath was contained in a room whose temperature was maintained to within 0.2°F during the time a measurement was taken, although some early measurements were made in a room controlled only to within 1°F. The introduction of the sample into the calorimeter caused the internal temperature of the calorimeter to rise until the heat loss to the bath was equal to that supplied by the sample. The change in resistance of the Wheatstone bridge in the calorimeter was observed until equilibrium was reached. After the measurement of the equilibrium resistance, the sample was removed and a current was introduced into a calibrating heater, within the calorimeter, in an amount sufficient to cause nearly the same change of bridge resistance as did the sample.

Table 2.1—Description of Samples Used to Determine the Half Life of Po^{210}

Sample	Mount	Initial watts	Method of deposition
1	Pt	0.47891 ± 0.00005	Electrodeposition
2	Pt	0.0165429 ± 0.0000004	Electrodeposition
3	Pt	0.25586 ± 0.00001	Volatilization
4	Pt	0.28334 ± 0.00002	Volatilization
5	Inside hollow sphere	1.14697 ± 0.00004	Volatilization

The heater resistance was concurrently measured, and the power output of the heater was taken to be the power output of the sample after the heater power was linearly corrected for the difference in the bridge unbalance between the sample and the heater.

A description of the five samples used for the determination of the half life is shown in Table 2.1.

A list of the half lives obtained from these samples and the calorimeters used for each determination is given in Table 2.2.

Each half life was calculated from the respective decay constant which was determined by a least-squares fit of the determinations of the power output of the sample and the times at which the equilibria were reached.[30]

The effect of the probable errors was such that as long as experimental conditions were duplicated for every power determination, the half life was more accurate than the power determinations and approached the precision of the power determinations. The grand mean value of the half life was then computed from the six individual values which were determined. In this procedure each value of the half life was weighted in an inverse proportion to the square of its probable error. This work resulted in a more precise determination of the half life of Po^{210} than any value previously reported.

Table 2.2—Values of the Half Life of Po^{210}

Calorimeter	Sample	Time covered by measurements, days	No. of observations	Half life, days	Probable error, days
A	1	250	19	138.391	0.023
B	3	617†	32	138.401	0.012
B	4	357	32	138.408	0.014
B	5	352	36	138.4059	0.0068
C	2	153	20	138.410	0.024
D	4	105	24	138.314	0.024
		Grand mean average		138.4005 ± 0.0051 days	

† Only two measurements were taken after the 284th day.

3. Po^{210} RADIATION

The types of radiation associated with the decay of Po^{210} are alpha, gamma (0.8-Mev energy), and X. The predominant and best known radiation, alpha, has been known since the discovery of polonium. The gamma radiation associated with the decay of polonium has been known only a comparatively short time. Reports of a fine structure of the polonium alpha spectrum, consisting of several groups[32] of less than 5.298 Mev energy, stimulated a search for the corresponding gamma rays from the lead nucleus. Although it was later learned that the observed fine structure originated from other causes,[33] the search for the corresponding gamma rays led to much information on the gamma-ray and X-ray spectra associated with the decay of polonium.

3.1 *Alpha Radiation.* (a) *General.* The alpha radiation from Po^{210} consists of two parts. The first and best known has an energy of 5.298 Mev, and the second has an energy of approximately 4.5 Mev. The 0.8-Mev difference between these alphas is accounted for in the emission of the 0.8-Mev gamma radiation which is observed from Po^{210}. The energy and range of the 5.298-Mev alpha particles have been under extensive investigation since their existence became known. The range of the alpha particles was of particular interest to the early investigators, although it was some time before it was realized that the range could not be determined uniquely because of the statistical fluctuation of the energy loss of the alpha particles as they passed through matter. When it was realized that the spread of energies was due to a fluctuation of the number of collisions and the energy loss per collision suffered by the alpha particles along their path length, new definitions of range became necessary. Actually, two range definitions have become accepted, mean range and extrapolated range. The mean range is specified from the number of alpha particles stopping in a small interval at a given distance from the source (in air at 760 mm Hg pressure and 15°C). The number of particles stopping in an interval will form a Gaussian distribution about some distance from the source. This distance is defined as the mean range, $\bar{R}$, and is illustrated as curve A in Fig. 2.1. The extrapolated range, R, is obtained by extending the linear portion of the straggling curve to the abscissa, as shown by curve B in Fig. 2.1.

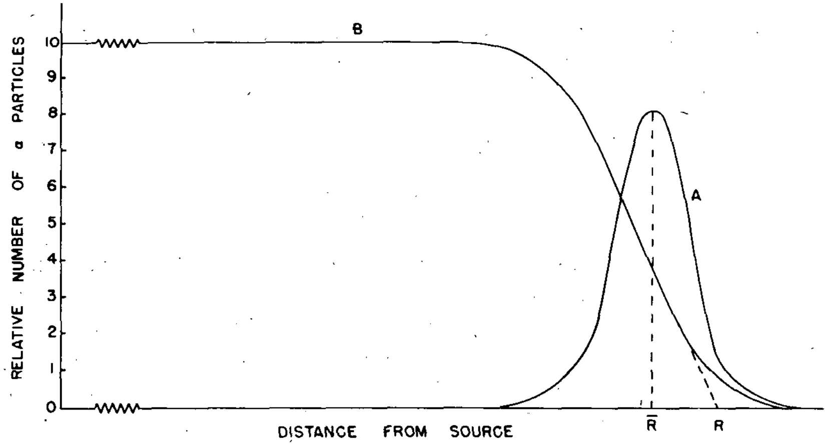


Fig. 2.1—Range of Po^{210} alpha particles.

In addition to the statistical fluctuation in the number of collisions and the energy lost per collision, other factors alter the range observed. If the range is determined in a cloud chamber, the range observed will be too short because very close to the end of the path the energy of the particles becomes too small to cause ionization, thus not leaving an observable track. If the range is determined, either visually or electronically, with a scintillator, the particles may not have sufficient energy near the end of their path to cause an observable event. An additional straggling of the range curve is caused by the energy loss of the alpha particles in escaping through the polonium film. Only atoms lying on the surface of the sample contribute to the true range measurement.

(b) *Energy of* Po^{210} *Alpha Particles*. Absolute measurement of the energy of the main group of Po^{210} alpha particles was made by Rosenblum and Dupouy[34] and by Lewis and Bowden.[35] The Lewis and Bowden value was recalculated from their value of the alpha-particle energy of RaC′ and the value for this alpha reported by Briggs[36] and Holloway and Livingston.[37] Lewis and Bowden reported the value of the polonium alpha energy as 5.2984 ± 0.0021 Mev. Recently, De Benedetti and Minton[38] have observed a lower-energy group of alpha particles from Po^{210}. This group of alphas was reported to have approximately 0.8 Mev energy less than the main group of alphas and to occur about once for every 10^5 alphas of 5.298 Mev energy.

The alpha-particle energies of Rosenblum and Dupouy,[34] Lewis and Bowden,[35] and Briggs[36] were determined by a magnetic deflection method. The lower-energy alphas found by De Benedetti and Minton[38] were measured in coincidence with the 0.8-Mev gammas by a pulse-height analyzer.

(c) *Range of Po^{210} Alpha Particles.* The range of the Po^{210} alpha particles is usually reported for standard conditions of temperature and pressure in air (15°C and 760 mm Hg pressure). Holloway and Livingston[37] report the mean range of the Po^{210} alphas as 3.842 ± 0.006 cm under standard conditions. They also report the extrapolated range as 3.870 ± 0.006 cm under the same conditions. This compares favorably with one of the earliest values for the maximum range of 3.77 cm reported by Levin[39] in 1906.

3.2 *Electromagnetic Radiations Associated with Po^{210}.* (a) *General.* Three electromagnetic radiations associated with Po^{210} decay are recognized at the present time, and these radiations have energies of 0.8 Mev and 80 and 10 kev. These gamma and X rays are the result of the daughter-lead nucleus being left in an excited state (0.8-Mev gammas), or are due to ionization of the electronic shell by the passage of the alpha particles, or are due to internal conversion of the 0.8-Mev gammas giving rise to characteristic X rays of lead.

(b) *Gamma Radiation.* The occurrence of gamma rays associated with Po^{210} decay was subject to controversy until comparatively recently. In 1914 Russell and Chadwick[40] reported observance of weak gammas (mass absorption coefficient of 215 in aluminum) from polonium after having taken care to remove any charged particles with a magnetic field. These apparent gammas were later suggested as being protons from alpha-particle collisions with nuclei of the air. As late as 1929, Curie and Joliot[41] reported that no gamma rays were emitted by polonium, although L X rays were observed from the silver support. Bothe and Becker[42] proved the existence of weak gamma rays from polonium in 1930. The gamma rays they detected can be associated with the 0.8-Mev gamma radiation that is presently recognized.

The energy of the 0.8-Mev gammas was reported as 0.803 ± 0.006 Mev by Alburger and Friedlander[43] in 1951 and as 0.804 ± 0.005 Mev by Pringle and coworkers[44] in 1952. The intensity of this gamma radiation has been reported as $1.8 \pm 0.14 \times 10^{-5}$ quantum/dis by Grace and coworkers,[45] and as $1.6 \pm 0.2 \times 10^{-5}$ quantum/dis by Riou.[46] This gamma radiation is the result of the change of the residual lead nucleus from the first excited state to the ground state.[43] Alpha particles of approximately the correct intensity and energy have been observed by De Benedetti and Minton[38] to confirm the existence of this excited state.

(c) *X Radiation.* The energy of the 80-kev X rays has been reported as 77 ± 2 kev by Pringle and coworkers[44] and as 76 ± 4 kev by Barber and Helm.[47] The intensity of this radiation has been reported to be $1.5 \pm 0.5 \times 10^{-6}$ quantum/dis by Grace and coworkers,[45] and as $1.6 \pm 0.5 \times 10^{-6}$ quantum/dis by Riou.[46] The exact origin of these X rays is still somewhat in doubt, although it is fairly well established that they are K X rays of the residual lead nucleus. Grace and coworkers[45] report a soft beta radiation of $1.2 \pm 0.3 \times 10^{-6}$ beta/dis, indicating that the 80-kev X rays are chiefly the result of an internal conversion of the 0.8-Mev gammas. They report an internal conversion coefficient of 6.7 ± 1.7 per cent for this process. However, Pringle and coworkers[44] report that less than 1 per cent of the 80-kev K X rays are in coincidence with the 0.8-Mev gammas, indicating that a major portion of these K X rays are produced by a self-ionization caused by the passage of the alpha particles through the electronic configuration of the residual lead nucleus. The exact method of production of these 80-kev X rays remains to be determined, whether by alpha ionization, internal conversion of the 0.8-Mev gammas, or nuclear cascade as suggested by Chang.[32] However, the theory that these radiations were of nuclear origin was discredited by Wadey[33] when he failed to confirm the fine structure of the alpha radiation observed by Chang.

Another group of very soft (10-kev) X rays has been observed to be associated with the decay of Po^{210}. These were suggested by Joliot and Curie[48] to be L and M X radiation from polonium. They later reported the intensity of the L X radiation as 1.5×10^{-3} quantum/dis (see reference 49). Recent reports have verified the existence of this radiation and have indicated that the L and M X radiation originates either by the ionization of the residual lead nucleus by the escaping alpha particles or by internal conversion of the 0.8-Mev gammas. Rubinson and Bernstein[50] claim to have proved the existence of lead L X rays having a yield of $2.93 \pm 0.44 \times 10^{-4}$ quantum/dis, and they observed what they presumed to be M X rays from polonium sources. Riou[46] in 1952 reported the intensity of the lead L X rays as $2.2 \pm 0.5 \times 10^{-4}$ quantum/dis.

4. SUMMARY

The radiation associated with the decay of Po^{210} is of three types, alpha, gamma, and X. The alpha radiation falls into two groups, the main group at 5.298 Mev energy and a weaker group of approximately 0.8 Mev less energy. The gamma radiation consists of a line at 0.803 Mev. One or more lines of X radiation occur at approximately 77 and 10 kev. Of these three radiations, only the alpha particles originate with polonium. The 0.8-Mev gammas are the result of the decay of an excited state of the lead nucleus. The X rays result when vacancies in the residual lead electronic configuration are filled. These vacancies may be the result of either ionization by the escaping alpha particles or by internal conversion of the 0.8-Mev gammas. Beta particles have been reported which presumably arise from internal conversion of the 0.8-Mev gammas. The existence of these particles has not been well substantiated. A detailed listing of the radiation associated with Po^{210} is shown in Table 2.3.

Table 2.3—Radiation Associated with Po^{210} Decay

Type of radiation	Energy, Mev	Abundance, %	Origin
α	5.298 ± 0.002	~ 100	α decay of Po
α_1	~ 4.5	~ 0.001	α decay of Po to excited state Pb^{206}
γ	0.804 ± 0.005	$1.8 \pm 0.14 \times 10^{-5}$ gamma/dis	Decay of Pb^{206} excited state
X rays	0.077 ± 0.002	$1.5 \pm 0.5 \times 10^{-6}$ X ray/dis	Lead K and L X rays, self-excitation or internal conversion
X rays	0.01 to 0.015	$2.93 \pm 0.44 \times 10^{-4}$ X ray/dis	
β	0.804 − K and L X-ray binding energy		Internal conversion of 0.8-Mev gammas

REFERENCES

1. P. Curie and M. Curie, Compt. rend., 127: 175-178 (1898).
2. E. Marsden and R. H. Wilson, Nature, 92: 29 (1913).
3. E. Marsden and T. Barratt, Physik. Z., 13: 196 (1912).
4. T. Barratt, Radium, 9: 81 (1912).
5. O. Hahn and L. Meitner, Physik. Z., 10: 703 (1909).

6. K. Fajans, Physik. Z., 12: 376 (1911).
7. K. Fajans, Physik. Z., 13: 703 (1912).
8. E. Rutherford, Trans. Roy. Soc. London, A204: 188, 204, 206 (1905).
9. H. Geiger and E. Marsden, Physik. Z., 11: 9 (1910).
10. H. Geiger, Phil. Mag., 21: 201 (1911).
11. H. Geiger and E. Marsden, Physik. Z., 11: 7 (1910).
12. E. Rutherford and H. Geiger, Phil. Mag., 22: 621 (1912).
13. E. Rutherford, Proc. Roy. Soc. London, A73: 493 (1904); Phil. Mag., 8: 636 (1904).
14. W. H. Bragg and R. Kleeman, Phil. Mag., 10: 318 (1905).
15. E. Rutherford, Phil. Mag., 12: 141 (1906).
16. W. W. Meinke, A. Ghiorso, and G. T. Seaborg, Phys. Rev., 75: 314 (1949).
17. J. M. Hollander, I. Perlman, and G. T. Seaborg, Revs. Mod. Phys., 25: 596 (1953).
18. D. G. Karraker, A. Ghiorso, and D. H. Templeton, Phys. Rev., 83: 390 (1951).
19. D. G. Karraker and D. H. Templeton, Phys. Rev., 81: 510 (1951).
20. D. H. Templeton, J. J. Howland, and I. Perlman, Phys. Rev., 72: 766-771 (1947).
21. E. L. Kelly and E. Segrè, Phys. Rev., 75: 999 (1949).
22. J. M. Hollander, I. Perlman, and G. T. Seaborg, Revs. Mod. Phys., 25: 595-596 (1953).
23. "Gmelins Handbuch der anorganischen Chemie," System No. 12, Polonium und Isotope, pp. 39-40, Verlag Chemie, G.m.b.H., Berlin, 1941.
24. M. Curie, Compt. rend., 142: 273-274 (1906).
25. M. L. Curtis, Phys. Rev., 92: 1489 (1953).
26. W. H. Beamer and W. E. Easton, J. Chem. Phys., 17: 1298 (1949).
27. W. H. Beamer and W. E. Easton, Half Life of Polonium, Report LAMS-418, Sept. 9, 1946.
28. L. V. Coulter, Progress Report MLM-M-1302, May 16–31, 1944.
29. D. C. Ginnings, A. F. Ball, and D. T. Vier, J. Research Natl. Bur. Standards, 50: 75 (1953).
30. J. F. Eichelberger, K. C. Jordan, S. R. Orr, and J. R. Parks, Calorimetric Determination of the Half Life of Po^{210}, Phys. Rev., 96: 719-721 (1954).
31. E. Rutherford and H. Robinson, Phil. Mag., 25: 312 (1913).
32. W. Y. Chang, Phys. Rev., 69: 60 (1946).
33. W. G. Wadey, Phys. Rev., 74: 1846 (1948).
34. S. Rosenblum and G. Dupouy, J. phys. radium, 4: 262 (1933).
35. W. B. Lewis and B. V. Bowden, Proc. Roy. Soc. London, A145: 235 (1934).
36. G. H. Briggs, Proc. Roy. Soc. London, A157: 183 (1936).
37. M. G. Holloway and M. S. Livingston, Phys. Rev., 54: 18 (1938).
38. S. De Benedetti and G. H. Minton, Phys. Rev., 85: 944 (1952).
39. M. Levin, Physik. Z., 7: 520 (1906).
40. A. S. Russell and J. Chadwick, Phil. Mag., 27: 112 (1914).
41. I. Curie and F. Joliot, Compt. rend., 189: 1270 (1929).
42. W. Bothe and H. Becker, Z. Physik, 66: 307 (1930).
43. D. E. Alburger and G. Friedlander, Phys. Rev., 81: 523 (1951).
44. R. W. Pringle, H. W. Taylor, and S. Standil, Phys. Rev., 87: 384 (1952).

45. M. A. Grace, R. A. Allen, D. West, and H. Halban, Proc. Phys. Soc. London, A64: 493 (1951).
46. M. Riou, J. phys. radium, 13: 244 (1952).
47. W. C. Barber and R. H. Helm, Phys. Rev., 86: 275 (1952).
48. F. Joliot and I. Curie, Compt. rend., 190: 1292 (1930).
49. I. Curie and F. Joliot, J. phys. radium, 2: 20 (1931).
50. W. Rubinson and W. Bernstein, Phys. Rev., 86: 545 (1952).

Chapter 3

PHYSICAL PROPERTIES OF POLONIUM

By James M. Goode

1. INTRODUCTION

The accurate measurement of the properties of polonium is difficult because of the intense radioactivity of the element; in addition, early workers were handicapped by the necessity of working with minute amounts of impure material. Consequently many of the physical constants reported in the literature are the result of calculations based on the known properties of neighboring elements in the periodic table. Direct measurements of a considerable number of the physical properties of polonium have been made at the Dayton Project and at Mound Laboratory. These include the determination of density, melting point, vapor pressure, heat of vaporization, studies of the optical spectrum and the crystal structure of the element, and measurements of the electrical resistivity and the Hall effect. The physical properties which have been determined are related directly or indirectly to the preparation of polonium; for example, studies of the vapor pressure have led to methods of preparing high-purity samples of polonium by fractional volatilization.

2. PHYSICAL CHARACTERISTICS OF POLONIUM

2.1 *Appearance.* Since the discovery of Po^{210}, some information has been acquired on the physical appearance of the metal. The early work on polonium was performed with extremely minute quantities of material of questionable purity, and, consequently, accurate observations of the physical appearance were impossible. The purification of comparatively large quantities of polonium by the irradiation of bismuth has permitted observations to be made on the purified metal, and it is now known that polonium is a silvery gray metal, much like lead in appearance, and is soft enough to be readily scratched with a dissecting needle.[1]

2.2 *Physical Behavior.* Polonium volatilizes readily in a vacuum and deposits in the form of a bright shiny mirror if the polonium is pure, although the deposit may be dull gray or black if the polonium preparation is impure. This mirror imparts, to quartz or glass, a blue-white glow that may be easily seen in a darkened room if sufficient polonium is present. As little as 10 mc may be observed if it is distributed over less than 1 mm length of a 0.5-mm I.D. tube or capillary. One curie is readily visible when distributed over 1 cm length of a 10-mm I.D. tube.

The action of high concentrations of polonium alpha particles on quartz or Pyrex glass causes the quartz or glass to "craze," or form small irregular cracks, on the surface exposed to the radiation. This crazing tends to weaken quartz or Pyrex containers; therefore caution must be exercised in handling old polonium ampoules. Crazing is not observed in small thin-walled X-ray capillaries made of either quartz or Pyrex, although these capillaries may collapse under the bombardment of alpha particles and recoil atoms if the capillaries have been evacuated. The apparent anomaly in the difference in effects observed between thin-walled and thick-walled quartz or Pyrex glass under bombardment of alpha particles is not understood.

3. PHYSICAL CONSTANTS OF POLONIUM

3.1 *Allotropy and Transition Temperature.* The allotropy of polonium was first observed by Maxwell[2] as a result of an abrupt change in the electrical resistivity near 100°C. This abrupt change was interpreted as the transformation of polonium from a low-temperature (or alpha) phase to a high-temperature (or beta) phase. Maxwell observed that the two phases coexisted for long periods of time over a wide range of temperature. The possibility that the hysteresis of the two phases over a wide temperature range was the result of a slow reaction rate was investigated and discarded because no indication of a reverse (beta-to-alpha) transition was observed when a sample was held 15°C below the beginning of the alpha-to-beta transition for 4 hr.

The temperature range of the transition was estimated by Maxwell to be between 65 and 130°C. He observed that the transition temperature range was a function of the thickness of the polonium film; the thicker the film the lower the transition temperature range. A temperature range of 100 to 130°C was obtained for a sample estimated to be 350 atoms thick, and a sample 10,000 atoms thick displayed a temperature range of 65 to 85°C.

The temperature of this phase transition was investigated by Goode[3] with a single sample using X-ray diffraction procedures. The sample was isolated in an inert atmosphere (helium) and mounted on a gold-plated thin brass plate. Temperature measurements were made with a thermocouple which was soft-soldered to the brass plate at a position opposite the polonium. The sample consisted of 1.4 mg of polonium purified by fractional volatilization immediately before the experiment, and it was uniformly distributed over a $^5/_{16}$-in.-diameter circle. The sample was deposited on the brass plate by distillation from a quartz ampoule. The ampoule, with one end removed, was placed in a tantalum can and heated by an induction heater until the polonium was distilled onto the brass plate. The thickness of the deposited sample was approximately 300×10^{-5} cm, as compared to 1 to 25×10^{-5} cm for the samples used by Maxwell. The phenomena observed were estimated to have taken place within a volume restricted to a depth of 50×10^{-5} cm because of the lack of penetration of the X rays. The phase change was observed by recording the intensity of the strongest diffraction lines of the alpha or beta phase as the sample was heated or cooled. For this sample the transition of the high- to low-temperature phase began at 54 ± 1.5°C, and the reverse transition began at 18 ± 1.5°C. The transition was rapid at temperatures well beyond those limits but quite slow, although apparently continuing, at temperatures near the start of the transition.

3.2 *Crystal Structure.* The existence of the two phases of polonium suggested by Maxwell[2] was confirmed by Beamer and Maxwell[4,5] by X-ray diffraction studies. They reported the low-temperature (or alpha) phase as a simple cubic structure, O_h^1, and the high-temperature (or beta) phase as a simple rhombohedral structure, D_{3d}^5. The lattice parameter, unit-cell edge a_0, was 3.345 ± 0.002 A for the simple cubic structure (alpha phase), and the parameters of the rhombohedral structure (beta phase) were $a_0 = 3.359 \pm 0.002$ A, and α (interaxial angle) = 98°13′ ± 3′.

The samples for these experiments were prepared by successive vacuum distillation of 30 to 100 μg of polonium into a lithiaborosilicate glass (Corning #707) capillary, 0.3 to 0.4 mm in diameter with a 20-μ wall thickness. Samples prepared in this way yield excellent powder X-ray diffraction photographs.

The alpha and beta crystal-structure studies of Beamer and Maxwell[5] were based on powder diffraction photographs. Single-crystal diffraction patterns of the material were not obtained because the intense energy of polonium, both from alpha particles and from nuclear recoils, was sufficient to destroy any single crystal of usable size that was formed.

The crystal structure of polonium was first studied by Rollier and coworkers[6] by electron diffraction of a film approximately 100 A thick. Beamer and Maxwell[4] showed that the pattern that Rollier and coworkers obtained was due to a mixture of the alpha and beta phases of polonium.

A recent reevaluation of polonium X-ray data from Mound Laboratory[7] verifies the crystal structure determined by Beamer and Maxwell; however, the crystal lattice parameters were obtained with greater precision. The lattice parameter for the alpha phase was a_0 = 3.359 ± 0.002 A, and the lattice parameters for the beta phase were a_0 = 3.366 ± 0.002 A and $\alpha = 98°5' \pm 2'$. The beta phase may also be indexed in the hexagonal system of crystal notation as a_0 = 5.084 ± 0.003 A and c_0 = 4.943 ± 0.003 A. The above values are given for a temperature of 39 ± 15°C. These values were obtained by combining several sets of data from different samples and patterns. The most accurate values for the beta phase were calculated by the method of least squares.[8]

3.3 *Density.* The density of a comparatively massive sample of polonium was first measured by Maxwell[2] in 1946. He found the density of polonium to be 9.4 ± 0.5 g/cu cm. The measurement was made by centrifugally casting an "ingot" of polonium into a precalibrated capillary tube having a square end. The mass of the polonium was determined by calorimetric measurement of the heat evolved in the decay of the sample by a method similar to that used by Beamer and Easton[9] to determine the half life of polonium. The weight of the sample was calculated[1] to be 1201 ± 6 μg. The length of the ingot was measured after the sample cooled overnight in an oil bath at −50°C. The length of the ingot was approximately 2.44 mm over a bath-temperature range of 0 to 142°C. Maxwell was unable to detect the allotropic transformation that occurs in that temperature range. The density of 9.4 ± 0.5 g/cu cm measured by Maxwell would apply equally well to either the low- or high-temperature phase.

The density of polonium was measured by Brody[10] at the Dayton Project in 1947. Four determinations of the density were made; the experimental conditions were consistent except that the polonium was purified by fractional volatilization for the last three experiments. The experiments were performed with polonium which had been volatilized into a capillary tube. (The capillary tube was calibrated by successive additions of mercury, wherein the length of the mercury thread as well as the additional weight of the tube were measured.) The capillary tube, at a helium pressure of approximately 100 mm Hg, was mounted in a special furnace and heated to 400°C. The furnace was then mounted in a centrifuge and rotated at 2000 rpm for 20 min to drive the polonium into the end of the calibrated capillary tube where the polonium solidified. The tube was allowed to finish cooling, and the length of the polonium thread was measured with a traveling microscope at room temperature (approximately 25°C). The length of the thread could be measured by this means to within 0.1 per cent of its over-all length of approximately 5 mm. Although the measurement of the thread was carried out at room temperature, the temperature of the polonium was approximately 50°C above room temperature. This temperature differential was estimated from an observation that a like quantity of polonium had melted at a furnace temperature of 200°C, although the melting point of polonium had been established as approximately 250°C (see reference 2). After the length of the polonium thread had been measured, the quantity of polonium was determined by calorimetric measurement of the heat evolved in the polonium decay.

The density of the polonium, at 25°C room temperature, used in the first experiment was 8.69 ± 0.19 g/cu cm. This sample had not had high-volatility impurities removed. The densities for the polonium used in the rest of the measurements were 9.34 ± 0.14, 9.34 ± 0.21, and 9.20 ± 0.17 g/cu cm. These samples had both high- and low-volatility impurities removed by fractional volatilization. In view of the temperature under which these densities were measured, i.e., approximately 75°C, these densities refer to the high-temperature (or beta) phase of polonium since the phase change of alpha to beta polonium is essentially complete at 75°C (see reference 3).

The density of polonium can be computed also from X-ray data from knowledge of the volume of the unit cell and the number of atoms that occupy the unit cell. Clark[11] defines the unit cell as "... the smallest possible subdivision which has the properties of the visible macrocrystal and which, by the repetition or translation of itself in all directions, builds the crystal." On this basis the density of the alpha phase is 9.196 ± 0.006 g/cu cm. The X-ray density of the beta phase is 9.398 ± 0.006 g/cu cm (see reference 7), which is in agreement with the values found by Maxwell and Brody. The X-ray density represents the density of a perfect material having no distortions or vacancies in any of the atomic positions; it is the upper limit for any measured density. The deviation of the measured density from the X-ray density may indicate the degree of imperfection of the material, the lack of purity of the material, or any combination of both.

3.4 *Melting Point.* The melting point of polonium is listed by Gmelin[12] as approximately 1800°C. This value represents estimates and predictions but is not based on experimental evidence. Mendeléev[13] predicted the melting point of the material to be low but was no more specific.

The first experimental determination of the melting point of polonium was made by Maxwell,[2] who reported the melting point as 246 to 254°C. A lower value of 237°C was also reported for one experiment. These values were obtained from observations on the change of slope of the resistivity curve and by direct visual observation.

Determination of the melting point was also made at the Dayton Project and Mound Laboratory. Davis[14] reported a value of 262 ± 5°C for the melting point of polonium. This value was obtained by visual observation of a thin film of polonium heated in a furnace. The film became transparent at a furnace temperature of 262°C.

Another melting-point determination was made by Joy[15] by microscopic observation of a thin layer of polonium metal in a thin-walled quartz capillary mounted on a Kofler hot stage. Melting was observed to take place at 252 ± 2°C.

3.5 *Vapor Pressure*. The vapor pressure of polonium was measured by Brooks[16] in the temperature range of 438 to 745°C. The vapor pressure was measured with a quartz "sickle gauge" and mercury manometer. The polonium was contained within the body of the sickle gauge which was used as a measuring device for small pressures and pressure differences. A mercury manometer was used to measure the pressure of a balancing gas. An elaborate furnace system ensured proper temperature distribution; therefore the sample temperature was the lowest of the system. The polonium sample was very carefully purified before the experiment. The quartz sickle gauge was thoroughly outgassed before introduction of the sample.

The vapor pressure was determined by measuring the temperature of the sample with a calibrated thermocouple while measuring the pressure inside the sickle gauge by referring to the deflection of the gauge pointer at low pressures. At high pressures a balancing pressure of air was admitted around the sickle gauge. The pressure of this balancing gas was measured with a mercury manometer which was read with a cathetometer. The sickle gauge was returned to approximately null position with the balancing pressure, and a correction was made to the manometer reading to correct for the deviation of the sickle gauge from the null position. The sickle gauge was calibrated for slight deviations from the null position. The vapor pressure was measured at 10 temperatures between 438 and 745°C during the first 2 days of the experiment. Subsequent measurements showed a shift in the vapor pressure curve. Therefore the later measurements were not used to calculate the relation between vapor pressure and temperature.

The relation between vapor pressure and temperature was calculated by the least-squares method for a best fit to a linear curve of log P vs. 1/T. The pressure was measured to ±0.1 mm. Individual measurements were weighted in proportion to the square of the pressure. The relation between vapor pressure and temperature was found to be

$$\log P = \frac{-5377.8 \pm 6.7}{T} + 7.2345 \pm 0.0068$$

where T is the temperature in °K and P is the pressure in millimeters of mercury.

3.6 *Boiling Point.* From the equation of vapor pressure vs. temperature, the extrapolated boiling point is 962.04 ± 1.93°C.

3.7 *Heat of Vaporization.* From the vapor pressure vs. temperature relation, the latent heat of vaporization is 24,597 ± 31 calories/mole.

3.8 *Coefficient of Thermal Expansion.* The coefficient of thermal expansion of alpha polonium was measured by Brocklehurst and Vassamillet[17] at the Dayton Project. They measured the coefficient of expansion by observing the variation of the unit cell of alpha polonium with temperature. This was accomplished by obtaining X-ray diffraction powder photographs (in the back-reflection region for accuracy) of a sample at room temperature, at the temperature of boiling liquid nitrogen, and at the temperature of an alcohol–dry-ice mixture. The sample was contained inside a Dewar flask just above the surface of the coolant. A window covered with a thin sheet of mica permitted the entrance and exit of the X-ray beam. Brocklehurst and Vassamillet found a value for the coefficient of linear expansion of alpha polonium of $22.0 \pm 1.5 \times 10^{-6}$ cm/cm/deg.

Later work by Goode[18] at Mound Laboratory, using a similar method, resulted in three values of the linear coefficient of thermal expansion of alpha polonium. An average of the three values obtained by weighting inversely as the square of the probable error is $23.5 \pm 2 \times 10^{-6}$ cm/cm/deg over the temperature range of −196 to +30°C. These values of the coefficient of thermal expansion were obtained by observing the unit-cell length at room temperature and at the temperature of boiling liquid nitrogen. The temperature of boiling liquid nitrogen was attained by spraying the sample capillary with a fine spray of liquid nitrogen, thus keeping the sample at the boiling point of liquid nitrogen. An internal standard of a gold wire was used to determine the temperature of the sample at room temperature since the temperature of the sample would have been an unknown amount higher than its surroundings (in air) owing to the heat released in the decay of the polonium.

An earlier report on the coefficient of linear expansion of polonium was made by Beamer and Maxwell[5] as an incidental observation in connection with their X-ray work. They reported a value of $50 \pm 25 \times 10^{-6}$ cm/cm/deg for the coefficient of linear expansion of beta polonium. An anomalous value for the coefficient of linear expansion of alpha polonium, reported by Beamer and Maxwell, can be shown to have been due to another effect.[19]

3.9 *Electrical Resistivity.* The electrical resistivity of polonium was first measured by Maxwell[2] and by Maxwell and Beamer,[1] who observed the voltage drop across a thin film of polonium mounted between 30-mil tungsten electrodes which were sealed through the end of a Pyrex-glass electrode holder. The film of polonium was vaporized onto the glass electrode holder. The voltage drop was measured with a potentiometer between two center electrodes while approximately 10 ma of current was passed between two end electrodes. The electrode holder was masked off before distillation of the polonium, except for a strip approximately 10 by 1½ mm which contained the tungsten electrodes, to ensure accurate deposition of the polonium film.

The polonium used for the resistivity measurements was first purified by electrodeposition (from a dilute nitric acid solution) onto a platinum foil. The foil was heated *in vacuo* with an induction heater to distill the polonium onto the glass electrode holder. The holder was then surrounded with helium and inserted into a furnace for observation of the resistivity of the polonium film as a function of temperature.

The quantity of polonium used in the experiment, between 15 and 400 μg, was determined by an alpha count of the electrode holder. The uniformity of two films that were deposited was observed with a special alpha pinhole camera. Densitometer traces of the camera films showed a uniform taper in the thickness of the deposit of 8 per cent in one case and 20 per cent in another. The error in the specific resistivity introduced by assumption of a uniform taper of 20 per cent is of the order of 3 to 4 per cent.

Five values of the electrical resistivity were obtained by this method. These values were converted to a temperature of 0°C with the experimentally determined thermal coefficient of electrical resistivity. For the alpha (or low-temperature) form of polonium, the average of five values of electrical resistivity at 0°C was 42 ± 10 μohm-cm. For the beta (or high-temperature) form of polonium, the average of five values at 0°C was 44 ± 10 μohm-cm.

A value of the electrical resistivity of polonium was obtained as an incidental measurement by Manring and Wehmeyer[20] of Mound Laboratory. They used a method very similar to that used by Maxwell and Beamer, except that printed platinum contacts on quartz were used instead of tungsten electrodes in glass. They found a value of 95.5 μohm-cm for the electrical resistivity of polonium.

The electrical resistivity was measured by Manring[21] at Mound Laboratory in 1949. The resistivity was measured by observing the change in Q of a tuned circuit as a ring-type sample of polonium was introduced into the primary driver-coil. The Q of an electrical circuit is defined as $\omega L/R$, where ω is the angular electrical frequency, L is the inductance, and R is the resistance of the coil plus any losses coupled into the coil by mutual inductance. The apparatus was calibrated with tantalum rings whose resistance per unit length was known.

The experiment was performed by shaping the polonium into the form of a ring on the inside surface of a quartz tube by volatilizing the polonium with a gas-oxygen torch and condensing it under a water-cooled brass collar. Observations were then made as the polonium ring contained in the quartz tube was inserted in the primary coil. When a discontinuous polonium ring was formed, no change in Q could be observed when it was inserted into the coil, thus showing that conduction in the quartz or conduction by ion currents was not measurable. The ring having the lowest resistivity, indicating the greatest homogeneity, was used. From this experiment the resistivity for the alpha (or low-temperature) phase of polonium was found to be 140 ± 10 μohm-cm at 20°C.

3.10 *Thermal Coefficient of Electrical Resistivity.* The thermal coefficient of electrical resistivity was determined by Maxwell[2] and by Manring[21] in connection with their resistivity measurements by observation of the resistivity as a function of temperature. Maxwell found the thermal coefficient (average of five values) to be 0.0046 ohm/ohm/°C for the alpha phase and 0.0070 ohm/ohm/°C for the beta phase of polonium. Manring found the thermal coefficient for the alpha phase (−56 to +68°C) to be 0.00421 ohm/ohm/°C.

3.11 *Hall Effect.* If a current, i_X, is passed through a sheet of metal in the X direction, and a magnetic field, H_Z, is applied along the Z axis, a voltage will appear along the Y direction of the metal. The production of this voltage and its magnitude is the Hall effect. From a determination of the Hall effect, information is obtained concerning the number, type, and mobility of the charge carriers in the metal. The Hall effect in polonium was studied by Manring and Wehmeyer[20] at Mound Laboratory in 1950.

The sample mount consisted of a quartz plate 2 cm long and 0.4 cm wide, with printed platinum strips for current electrodes at each end and with point-printed platinum contacts equidistant between the ends along the edges of the sample mount for the Hall voltage contacts. Polonium was distilled onto the plate from platinum foils in an induction-heated nickel boat. The sample consisted of 2.431×10^{-3} g of polonium.

The attempt to detect the Hall voltage was not successful. An increase in resistance of the polonium film with time was sufficient to mask the effect sought. Had the Hall voltage contacts been located exactly along an equipotential line, the increase in resistance would have had no effect; since this was not the case, a small voltage due to the current flow appeared between these contacts. This led to an upper limit of 0.03 mv for the Hall voltage. On the basis of this upper limit for the Hall voltage, the minimum number of current carriers was determined to be 3×10^{21} carriers/cu cm. Since there are 3×10^{22} polonium atoms per cubic centimeter, this indicates that there is at least one current carrier for 10 polonium atoms.

4. DIFFUSION OF POLONIUM INTO METALS

The diffusion of polonium into metals has long been subject to qualitative study. The first quantitative data were published by Hevesy and Obrusheva[22] in connection with the self-diffusion of lead. They measured a value of 1.5×10^{-10} sq cm/sec for the diffusion constant of polonium into lead at 310°C. Later Jedrzejowski[23] measured a value of 2.4×10^{-8} sq cm/sec for the diffusion constant of polonium into platinum at approximately 900°C.

The diffusion of polonium into metals was studied by Foster and Eyles[24] at Mound Laboratory, and approximate diffusion coefficients were determined for aluminum, stainless steel, and bismuth. The diffusion coefficients were determined by depositing the polonium between the center foils of a stack of four or six thin foils. These foils were sealed at the edges by clamping in a stainless-steel bomb, which was then placed in a preheated temperature-controlled furnace for a predetermined time. The foils were sealed in the bomb immediately after deposition of the polonium to minimize the spread of polonium.

The amount of polonium on a given surface was determined by a counting technique. The inside surfaces of the two center foils were counted last to ensure that the counts on the back surfaces of the center foils were due to diffusion and not to contamination spread in handling. The loss of polonium to the inside surfaces of the center foils was not sufficient to cause appreciable error in the diffusion constant.

The diffusion constant of polonium in aluminum was measured over a temperature range of 20 to 500°C. The diffusion constant was approximately 3×10^{-13} sq cm/sec at 20°C and 5×10^{-11} sq cm/sec at 500°C. The diffusion constant for stainless steel was approximately 1×10^{-12} sq cm/sec at 300°C and 5×10^{-11} sq cm/sec at 750°C. The diffusion constant for bismuth was approximately 5×10^{-11} sq cm/sec at 150°C and 5×10^{-10} sq cm/sec at 200°C.

5. OPTICAL SPECTRUM OF POLONIUM

The investigation of the optical spectrum of polonium was begun in 1910 by M. Curie and Debierne.[25] They concentrated the polonium from several tons of uranium ores and obtained approximately 0.1 mg of polonium in a 2-mg residue. Four lines from the spark spectrum of the residue were tentatively identified as polonium lines, a strong line at 4170.5 A and three faint lines at 4642.0, 3913.6, and 3652.1 A. The line at 4170.5 A has been confirmed as one of the persistent lines of polonium; the others have not been observed.[26] Another spark line was observed by Czapek[27] at 2450.0 A. Karlik and Pettersson[28] used a gaseous discharge, with hydrogen, helium, and neon acting as carriers, to find four lines tentatively identified as polonium lines. These lines had wavelengths of 2450.0, 2558.1, 3005, and 5665 A. The latter two lines were observed only with helium and hydrogen, respectively, and therefore were considered likely to be due to impurities.

The emission spectrum of polonium was investigated by Staniforth, Beasecker, and Economides[29] at the Dayton Project. Thirty-three lines assigned to polonium were observed. The spectrum was obtained by depositing polonium on small spectroscopically pure platinum foils and arcing these foils between carbon electrodes. The electrodes were contained within a sealed sample chamber having quartz windows to prevent the spread of contamination. The electrode chamber was flushed with argon to eliminate cyanogen bands in the ultraviolet region. It was observed that the use of the argon atmosphere resulted in a loss of sensitivity. (The wavelengths of the lines were measured to an accuracy of ±0.05 A for the lower wavelengths and to ±0.10 A for the higher wavelengths.) The lines observed that were attributed to polonium are listed in Table 3.1.

Table 3.1 — Wavelengths of Polonium Lines Observed by Staniforth, Beasecker, and Economides

Wavelength, A	Comment	Wavelength, A	Comment
2406.61		2725.34	
2426.45		2737.50	
2439.39		2761.91	
2450.09	Strong	2800.28	
2477.32		2823.73	
2483.96		2849.18	
2490.4		2936.59	
2520.28		2972.92	
2538.32		2989.70	
2546.48		2994.79	
2546.71		3003.25	Strong
2558.11	Strong	3004.09	
2598.28		3008.19	
2599.55		3015.40	
2602.07		3026.341	
		3045.69	
		3054.73	
		3205.67	

The work on the spectrum of polonium was continued at Mound Laboratory by Charles and coworkers.[30] Two source types were used to obtain the spectrum: An enclosed source, similar to that used by Staniforth and coworkers, was used to obtain the spark spectra. The electrodes used were high-purity carbon, with the polonium deposited directly on the electrodes. The spectrum was obtained on a Baird 3-meter spectrograph; an A.R.L. Multisource was used for the excitation voltage. The spectrum of polonium was also obtained using an electrodeless discharge as a potential source. Leads from a high-frequency (approximately 30, or 400, Mc/sec) generator (Chap. 9, Sec. 4.8) were wrapped around a sealed quartz ampoule of polonium plus carrier gas, or polonium alone. If the ampoule was heated to approximately 400°C, a carrier gas to sustain the discharge was not needed. The polonium was purified by fractional volatilization before being put in the ampoule; the purity was estimated to be greater than 99 per cent. The spectra from this source were recorded between 1920 and 9375 A with a Baird 3-meter spectrograph and consisted of line spectra superimposed on the band spectra of the polonium molecule.

Spectrograms were measured on a linear comparator, and wavelengths were calculated by linear interpolation. They were then improved by use of a correction curve constructed from lines of impurity elements. The results of the measurements are given in Appendix A, giving visual estimates of intensity, occurrence of the line, wavelength, frequency, and classification. All classifications given are in the spectrum of Po I.

A partial analysis of the line spectrum has been made, starting from the discovery that two common differences exist among the five strongest lines. With this start the analysis proceeded by a search for differences. The correctness of the analysis has been indicated by excellent agreement between theoretically predicted intervals in the fundamental configuration as well as by the excellent fit of electrostatic and spin-orbit parameters derived from the analysis with those for O I, S I, Se I, and Te I. The proposed energy levels of Po I derived from the analysis are presented in Appendix B. The levels from $6p^3$ (4^0_S) np are regarded as tentative. Because of the expected overlap of levels from 6d with those from 7s, it has not been possible to assign configurations to odd levels except for those arising from $6p^3$ (4^0_S) ns.

The ionization potential of Po I has been estimated from the energy levels by making certain assumptions about the identities of levels 7^0_2 and 8^0_1. These two levels fit well the expected positions and separation of the second series member $6p^3$ (4^0_S) 8s. With this assumption, one can estimate the absolute value of the ground level $6p^4$ $^3P^1_2$. The result is 67,980 cm^{-1}, corresponding to an ionization potential of 8.43 volts for the neutral polonium atom.

6. MOLECULAR SPECTRUM OF POLONIUM

By George W. Charles[31]

There has been no reference to the molecular spectrum of polonium in the literature. Early in the study of the polonium spectrum at Mound Laboratory, a molecular spectrum was observed. When a problem of the assay of mixtures of Po^{208} and Po^{209} arose in 1951, the problem of the molecular spectrum was reexamined. A systematic study was made of the discharge conditions under which bands were obtained. As a result of these studies and of the isotope assay problem, numerous spectrograms became available with well-developed bands of Po_2^{210} and of mixtures of Po_2^{208} and $Po^{208}\,Po^{209}$.

The spectra were excited by radio-frequency oscillations. Good results were obtained at frequencies of 10 and 30 Mc/sec. In most cases polonium alone was used in the discharge tube. The tubes were heated to about 400 to 500°C. It was observed that the molecular spectrum was well developed when the discharge had a deep blue color, whereas the line spectrum predominated when the discharge was purple. Spectrograms were measured with a Bausch & Lomb Spectrum Measuring Magnifier. Wavelengths were calculated by linear interpolation and corrected by using known wavelengths of lines of polonium and of impurities. It is estimated that the measurements are accurate to ±0.3 A, corresponding to ±2K at the short-wavelength end of the spectrum and to ±1K at the long-wavelength end. The heads are very numerous and are degraded to the red. The principal heads are listed in Appendix C, which shows intensity (visual estimate), wavelength, and frequency. Heads belonging to the same transition in the different isotopes are listed on the same line.

Most of these bands have been put in an array which is well represented by the equation

$$v = 25{,}149 + 108.4\,(v' + \tfrac{1}{2}) - 0.43\,(v' + \tfrac{1}{2})^2 - 156.2\,(v'' + \tfrac{1}{2}) + 0.36\,(v'' + \tfrac{1}{2})^2 \qquad (3.1)$$

The energy levels of the lower state are listed in Appendix D, and those of the upper state are listed in Appendix E. Appendix F lists calculated and observed isotope shifts for some of the bands. The excellent agreement between observed and calculated isotope shifts lends support to the identification of the emitter as a diatomic molecule of polonium and to the correctness of the array and the constants determined from it. There is still the possibility (although remote) that the emitter is a diatomic molecule of ionized polonium. This question could be settled by a rotational analysis. The dissociation potential of the molecule has been estimated by linear extrapolation to band convergence. The result is 2.03 volts, obtained on the assumption that the neutral molecule in the ground state dissociated into two atoms in the ground state ${}^3P_2^1$.

REFERENCES

1. C. R. Maxwell and W. H. Beamer, Physical Properties and Crystal Structure of Polonium, Report LA-604, Aug. 30, 1946.
2. C. R. Maxwell, J. Chem. Phys., 17: 1288 (1949).
3. J. M. Goode, The Temperature of the Phase Transition of Polonium, Report MLM-615, Oct. 1, 1951.
4. W. H. Beamer and C. R. Maxwell, J. Chem. Phys., 14: 569 (1946).
5. W. H. Beamer and C. R. Maxwell, J. Chem. Phys., 17: 1293 (1949).
6. M. A. Rollier, S. B. Hendricks, and L. R. Maxwell, J. Chem. Phys., 4: 648 (1936).
7. J. M. Goode, A Redetermination of the Lattice Parameters of Polonium, Report MLM-808, Jan. 30, 1953.
8. J. B. Scarborough, "Numerical Mathematical Analysis," Johns Hopkins University Press, Baltimore, 1930.
9. W. H. Beamer and W. E. Easton, J. Chem. Phys., 17: 1298 (1949).
10. B. Brody, Density of Metallic Polonium, Report MLM-230, Nov. 9, 1948.
11. G. L. Clark, "Applied X Rays," 3d ed., p. 237, McGraw-Hill Book Company, Inc., New York, 1940.
12. "Gmelins Handbuch der anorganischen Chemie," System No. 12, Polonium und Isotope, p. 66, Verlag Chemie, G.m.b.H., Berlin, 1941.
13. D. Mendeléev, J. Chem. Soc., 55: 649 (1889).
14. R. Davis, Progress Report, Report MLM-M-583, June 1–30, 1946.
15. E. F. Joy, Quarterly Report for General Research, Report MLM-443-1, p. 42, January, February, and March, 1950.
16. L. S. Brooks, The Vapor Pressure of Polonium, Report MLM-189, Sept. 13, 1948.
17. R. E. Brocklehurst and L. F. Vassamillet, The Coefficient of Expansion of Polonium, Report MLM-112, May 26, 1948.
18. J. M. Goode, Report for General Research, Report MLM-484-1, p. 55, Apr. 1 to Aug. 7, 1950.
19. J. M. Goode, Metal-Polonium Compounds, Report MLM-677, p. 7, Apr. 1, 1952.
20. E. R. Manring and D. B. Wehmeyer, Report for General Research, Report MLM-509, p. 17, Aug. 7 to Oct. 30, 1950.
21. E. R. Manring, The Electrical Resistivity of Polonium, Reports from Session XIV, General Information Meeting, Oak Ridge, Tennessee, Report TID-280, p. 61, Oct. 24, 25, and 26, 1949.
22. G. Hevesy and A. Obrusheva, Nature, 115: 674 (1925).
23. H. Jedrzejowski, Acta Phys. Polon., 2: 137 (1933).
24. K. W. Foster and T. E. Eyles, Diffusion of Polonium Through Aluminum, Stainless Steel, and Bismuth, Report MLM-569, July 1, 1951.
25. M. Curie and A. Debierne, Compt. rend., 150: 386 (1910).

26. G. W. Charles, private communication, Oct. 14, 1953.
27. A. Czapek, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt IIa., 139: 593 (1930).
28. B. Karlik and H. Pettersson, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa., 143: 379 (1934).
29. R. A. Staniforth, D. R. Beasecker, and M. Economides, Progress Report, Report MLM-M-673, p. 7, Sept. 16–30, 1946.
30. G. W. Charles, G. Pish, and D. L. Timma, A Preliminary Description and Analysis of the Spectrum of Polonium, Report MLM-941, Jan. 28, 1954.
31. G. W. Charles and D. L. Timma, Vibrational Analysis of the Molecular Spectrum of Polonium, Report MLM-1004, Aug. 26, 1954.

Chapter 4

CHEMICAL PROPERTIES OF POLONIUM

By Harvey V. Moyer

1. INTRODUCTION, PREDICTED PROPERTIES

Mendeléev[1] predicted the existence of polonium about 10 years before its discovery. He named it "divi-tellurium" (Dt), and, from its position in Group VI in the periodic table, he characterized it as chemically analogous to tellurium with an atomic weight of 212. He predicted that the element would be low-melting, crystalline, nonvolatile, gray in color, and would have a density of about 9.3. It should form an oxide, DtO_2, which should exhibit both acidic and basic properties. Strong oxidizing agents should produce the unstable oxide, DtO_3. If the hydride should form, it would be less stable than H_2Te. It should be more metallic than tellurium but less so than bismuth.

The predicted physical properties agree fairly well with the observed properties except that it is considerably more volatile than predicted by Mendeléev. Its chemical properties were predicted with fair accuracy. An unstable hydride of polonium has been reported by Paneth and Johanssen[2] and others, but the predicted unstable oxide, PoO_3, has not been observed. The existence of the hydride of polonium has not been demonstrated at Mound Laboratory.

2. POLONIUM OXIDE

Polonium dioxide, PoO_2, is the only oxide of polonium which has been prepared and characterized. Martin[3] prepared a stable oxide of polonium and proved its formula to be PoO_2. Polonium oxide was also prepared by Moulton and Farr,[4] who reported the same formula. Martin purified samples of 5 to 10 curies of polonium by repeated volatilizations *in vacuo* and measured the volume of dry oxygen, at approximately 1 atm pressure, which combined with known quantities of polonium at temperatures ranging from 200 to 432°C. The volume of oxygen which

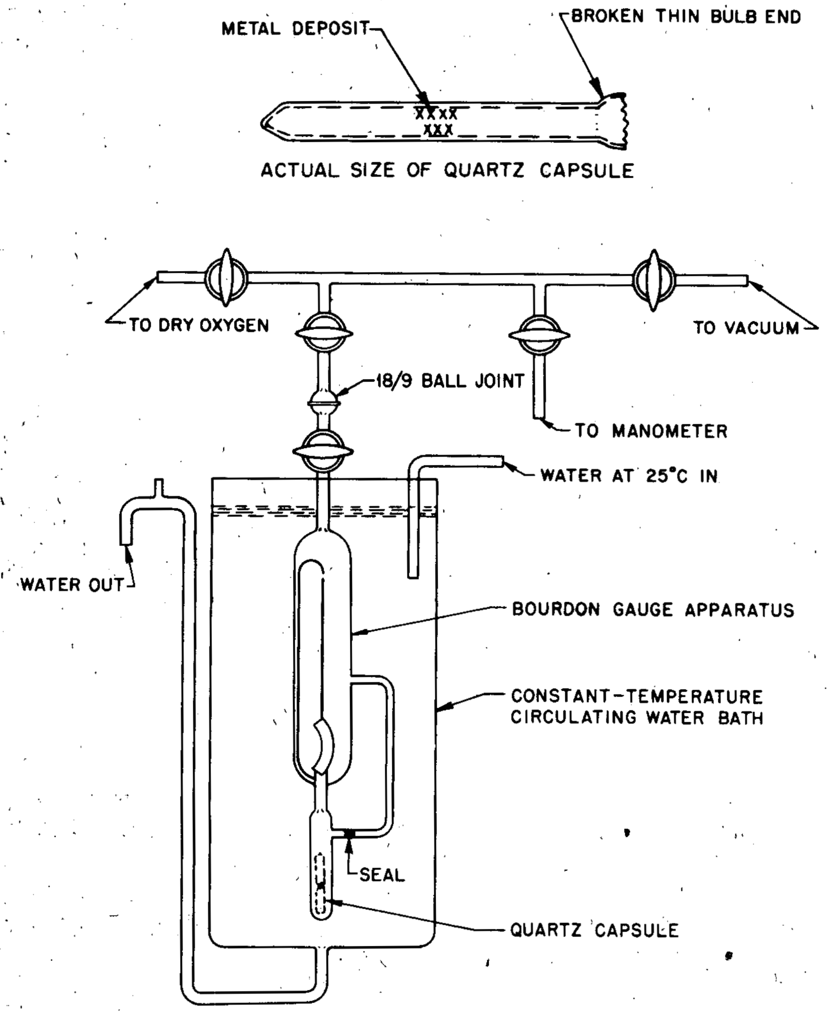


Fig. 4.1—Apparatus for preparing polonium dioxide.

combined with the polonium was measured at 25°C by use of a Bourdon gauge in the apparatus shown in Fig. 4.1. The reaction is slow in dry oxygen at room temperature but is rapid at 300°C. Changes in the pressure of oxygen were observed after heating the samples from 1 to 6 hr, and the heating procedure was repeated until the pressure of oxygen became constant. Results of three determinations are summarized in Table 4.1. The quantity of polonium was determined calorimetrically.

X-ray diffraction analyses were made on two preparations of polonium dioxide, one prepared by the oxidation of elemental polonium and the other by heating polonium nitrate. In both cases it was found that the dioxide exhibited two crystalline forms, a tetragonal structure which changed in a few days to a cubic fluorite type of crystal with the lattice parameter $a_0 = 5.59$. The cubic form has a theoretical density of 9.18 g/cu cm, and the radius of the Po^{+4} ion is 1.02 A. Polonium dioxide was stable when heated in oxygen, at 1 atm, up to a temperature of 900°C. No evidence was found to indicate the formation of polonium trioxide. Under the conditions of the experiments no polonium monoxide was formed.

Table 4.1—Summary of Three Determinations of the Formula of Polonium Dioxide

Conditions	μmoles of O_2 consumed	μmoles of Po combined	Ratio O/Po
Heated a total of 7.5 hr at 200 to 250°C	10.7	11.28	1.90
Heated a total of 3 hr at 400 to 432°C	4.6	4.496	2.04
Heated a total of 9 hr at 300 to 310°C	9.4	9.335	2.02

3. POLONIUM CHLORIDES

Two chlorides of polonium have been prepared and characterized by Joy.[5] Preliminary work was done by LaChapelle and coworkers.[6] Two methods of preparing the chlorides of polonium were attempted in the preliminary work: (1) polonium dioxide was treated with carbon tetrachloride vapor as described by Dede and Russ,[7] and (2) a solution of polonium in concentrated hydrochloric acid was evaporated to dryness in the presence of carbon tetrachloride vapor. Joy[5] found that the most satisfactory method was the direct combination of metallic polonium with dry chlorine at 1 atm pressure and at temperatures ranging from 125 to 200°C. The apparatus used by Joy is shown in Fig. 4.2. Approximately 100 μg of polonium was used in each preparation. The pure metal, upon being heated in chlorine, changed color progressively from gray to brown to yellow. The yellow chloride was volatilized at about 390°C and condensed under an atmosphere of chlorine into well-

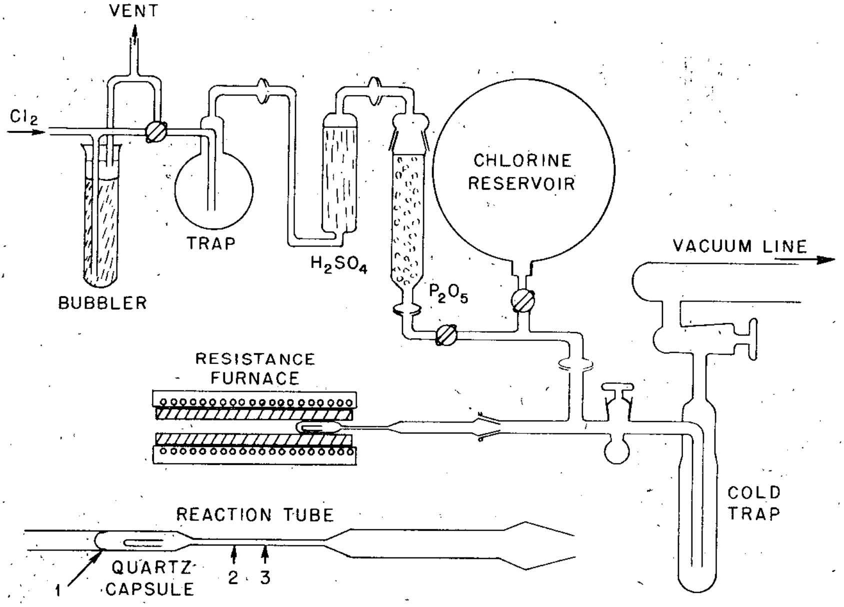


Fig. 4.2—Apparatus for preparing polonium-chlorine compounds.

formed yellow platelets. The yellow crystals were found to be $PoCl_4$. At lower temperatures and pressures of chlorine, a red compound was prepared which was shown to be $PoCl_2$. The red dichloride is more volatile than the tetrachloride and can be separated by careful volatilization in a capillary tube. A mixture of the red and yellow crystals is shown in Fig. 4.3. The pure yellow tetrachloride is shown in Fig. 4.4. The dichloride can be prepared by heating $PoCl_4$ to 200°C in an atmosphere of hydrogen. The reduction with hydrogen continues to the formation of a black residue which is presumed to be the metal. The black residue may again be converted to the yellow chloride by reheating the residue in an atmosphere of chlorine. The reactions may be expressed in the following equations:

$$Po + Cl_2 \rightarrow PoCl_2 \quad \text{(red)}$$

$$PoCl_2 + Cl_2 \rightarrow PoCl_4 \quad \text{(yellow)}$$

$$PoCl_4 + H_2 \rightarrow PoCl_2 + 2HCl$$

$$PoCl_2 + H_2 \rightarrow Po + 2HCl$$

Fig. 4.3 — $PoCl_2$ and $PoCl_4$ crystals.

Fig. 4.4 — $PoCl_4$ crystals.

Polonium tetrachloride cannot be sublimed except in the presence of excess chlorine. When heated to 260°C *in vacuo*, it undergoes partial dissociation to the dichloride.

The determination of the polonium content of each preparation of the chloride sealed in a capillary tube was made calorimetrically. The chloride content was determined by a potentiometric titration based on a micromethod by Glick.[8] The glass capillary tube containing the chloride sample was crushed under the surface of 0.2 ml of 0.2N nitric acid contained in the titration cell shown in Fig. 4.5. Immediate hydrolysis of the chloride occurred with the formation of a light yellow flocculent precipitate of hydrous oxide of polonium. Titration of the released chloride was made with 0.05N silver nitrate solution. Typical titration curves are shown in Fig. 4.6. A summary of the results of analyses of the red and yellow chlorides is shown in Table 4.2. A summary of the properties of the chlorides of polonium is shown in Table 4.3.

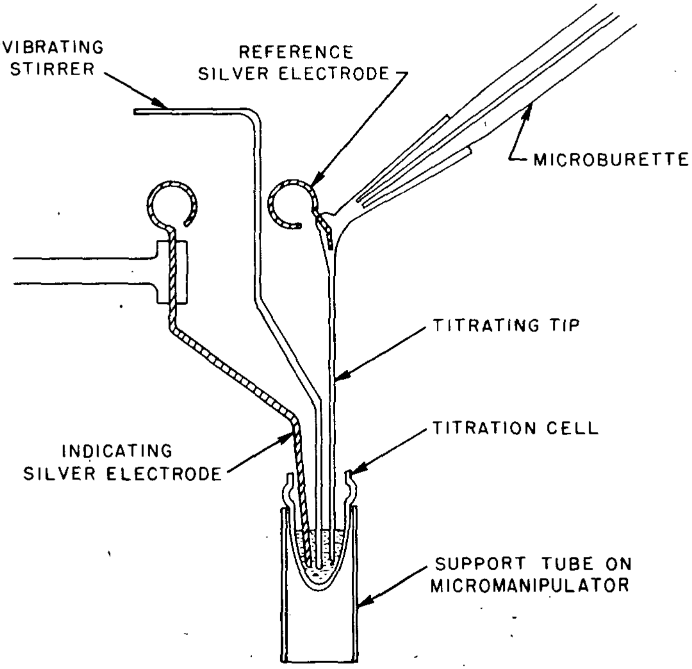


Fig. 4.5—Polonium chloride titration apparatus.

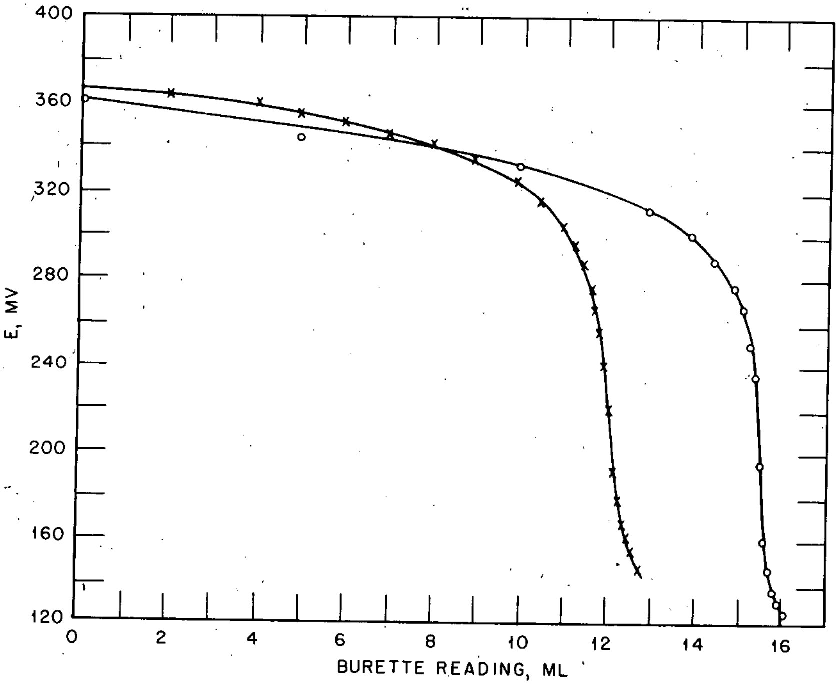


Fig. 4.6—Polonium chloride titration curves.

Table 4.2—Analysis of Polonium Chloride

Color	Po by calorimetric assay		Cl by titration, μmoles	Ratio Cl/Po
	Curies	μmoles		
Yellow	0.484	0.509	1.947	3.83
Yellow	0.596	0.626	2.465	3.94
Yellow	0.633	0.665	2.519	3.79
Yellow	0.523	0.549	1.981	3.61
			Av.	3.79
Red	1.012	1.063	2.144	2.02
Red	1.127	1.183	2.091	1.77
			Av.	1.90

Table 4.3 — Properties of Polonium Chlorides

	$PoCl_2$	$PoCl_4$
Color	Red	Yellow
Crystal system	Orthorhombic	Monoclinic or triclinic
Melting point (sealed tube), °C	170–180	294
Volatilization (vacuum), °C	190	220
Volatilization (atm of Cl_2), °C		390
Neutron emission, n/sec/curie	8.9×10^3	1.43×10^4

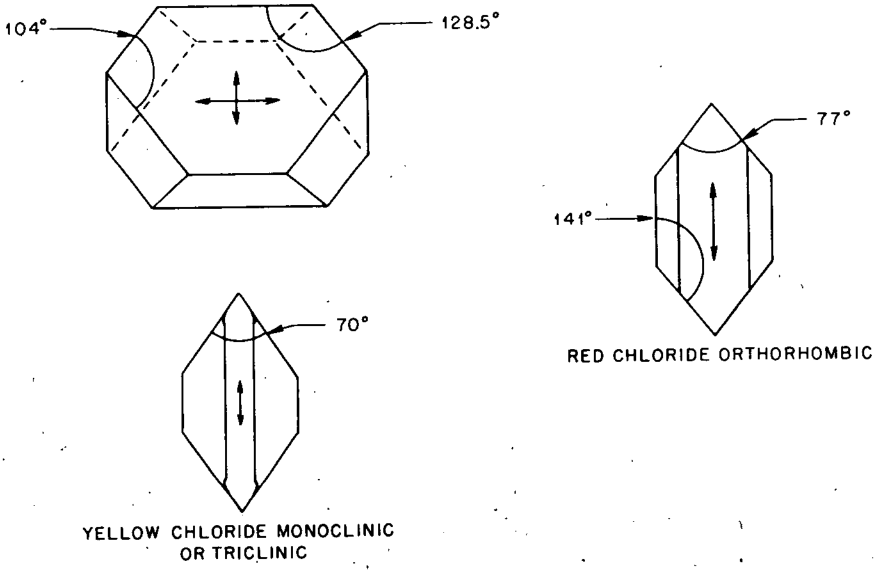


Fig. 4.7 — Crystalline habit of polonium chlorides.

The crystallographic characteristics of the crystals were difficult to determine because of the necessity of observing the crystals in a sealed tube. Refractive indices were not determined. Profile angles of typical crystals of the red and yellow chlorides were measured, with the results shown in Fig. 4.7. The yellow form was found in two crystalline forms as indicated, whereas only one form of the red chloride was observed. Both crystals are anisotropic and show parallel extinction as indicated. The melting points were determined with a polarizing microscope and a Kofler hot stage.

Exposure of samples of $PoCl_4$ to moist air results in the formation of needles which grow in every direction from the original crystals. This phase did not melt when heated up to 355°C, and its composition was not determined.

X-ray powder patterns of both polonium chlorides have been obtained and average line spacings have been calculated by Reynolds.[9] The powder pattern of $PoCl_2$ was indexed in the orthorhombic system and is similar to the powder pattern found in the dihalides of lead. The indexing gives a unit cell with the dimensions $a_0 = 4.331$ A, $b_0 = 8.944$ A, and $c_0 = 7.292$ A, and, if four molecules are assumed in a unit cell as in $PbCl_2$, the calculated density is 6.55 g/cu cm. The powder pattern of $PoCl_4$ was obtained and the average line spacings are reported by Joy.[5] The crystals were of lower symmetry than the dihalide; the lattice is either monoclinic or triclinic. A structure to fit the data has not been determined.

4. POLONIUM BROMIDE

Polonium tetrabromide was prepared by Joy,[10,11] who treated pure metallic polonium with dry bromine vapor at a pressure of 200 mm Hg. A reaction occurred when the polonium and bromine vapor were allowed to stand overnight at room temperature, and the reaction was complete after the tube was heated for 1 hr at 250°C. A product was volatilized at 360°C in the presence of bromine vapor and condensed in the cooler portions of the tube as dark red crystals ($PoBr_4$). The red crystals of polonium tetrabromide were also prepared by dissolving 0.5 curie of polonium in 0.015 ml of 40 per cent hydrobromic acid and evaporating the solution to dryness by passing a current of dry nitrogen over the solution at room temperature. X-ray diffraction studies showed that the tetrabromide prepared by dissolving polonium in hydrobromic acid was identical with the compound obtained by the direct combination of the elements. Typical $PoBr_4$ crystals are shown in Fig. 4.8.

The preparations of polonium tetrabromide were analyzed by calorimetrically determining the amount of polonium in a sealed capillary tube (containing the polonium tetrabromide sample) and then titrating the bromide potentiometrically by the same method used for the chloride.[8] Free bromine forms in the capillary tubes containing the samples, and as a consequence the first determinations of the tetrabromide gave low results. The theoretical bromide content of $PoBr_4$ was obtained by crushing the capillary tube under a 0.1N aqueous ammonia solution which reduced the bromine to bromide with the liberation of nitrogen. A precipitate of hydrated polonium dioxide formed which was separated by centrifugation, and this precipitate was washed in a

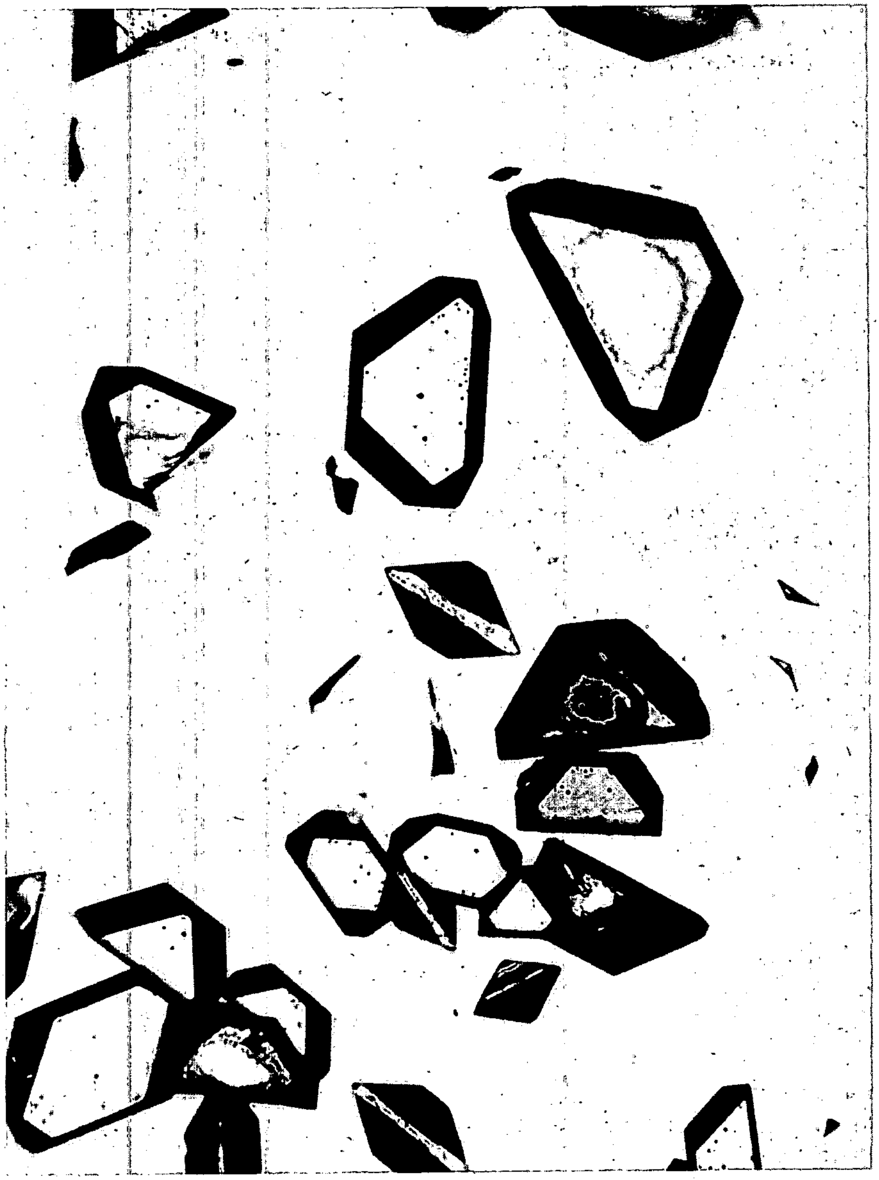


Fig. 4.8 — $PoBr_4$ crystals.

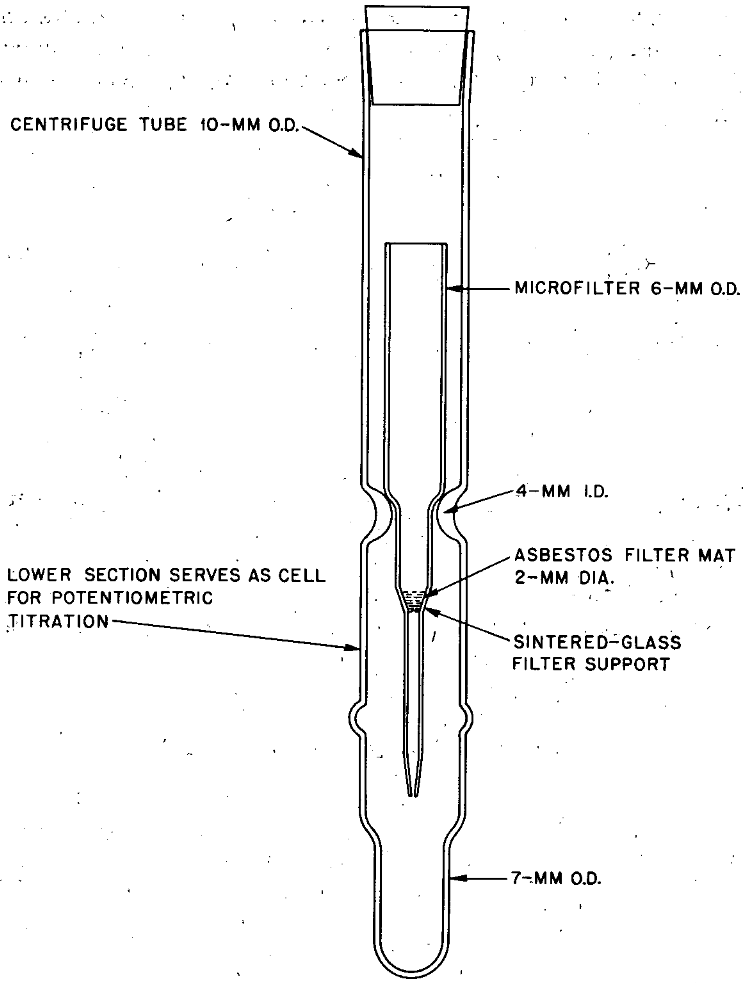


Fig. 4.9—Polonium tetrabromide centrifugation apparatus.

microfilter. The centrifuge tube and filter are shown in Fig. 4.9. Table 4.4 shows the results of the analysis of four samples of polonium tetrabromide.

Free hydrobromic acid is formed on hydrolysis of $PoBr_4$ according to the following reaction:

$$PoBr_4 + x\,H_2O \rightarrow PoO_2 . yH_2O + 4HBr$$

The free acid was titrated with a standard base, and the results confirmed the formula, $PoBr_4$. The melting point of $PoBr_4$ was observed to be 324 ± 2°C. Attempts to prepare polonium dibromide were unsuccessful.

Table 4.4—Analysis of Polonium Bromide

Po by calorimetric assay, μmoles	Br by titration with 0.05N $AgNO_3$, μmoles	Ratio Br/Po
1.145	4.512	3.94
0.827	3.227	3.90
0.501	1.994	3.98
0.745	3.039	4.08

The neutron emission[11] from three samples of polonium tetrabromide, confined in Pyrex capillary tubes, was measured; hence the results include a background from the (α,n) reaction with components in the glass. The observed values were 8.3×10^3, 9.4×10^3, and 6.3×10^3 neutrons/sec/curie. The observed neutron emission from polonium tetrabromide was somewhat lower than the average value of 1.4×10^4 neutrons/sec/curie from polonium tetrachloride.

5. POLONIUM IODIDE

Attempts were made by Marchi[12] to prepare compounds of polonium and iodine, but the ratio of polonium to iodine in the reaction mixtures varied over wide limits. No conclusive evidence of compound formation was obtained.

6. POLONIUM FLUORIDE

Since other members of the sulfur group form volatile hexafluorides by direct combination of the elements, it seems probable that polonium should react in a similar manner. The free energies[13] of formation of SF_6, SeF_6, and TeF_6, respectively, are 262,000, 246,000, and 315,000 calories/mole at 25°C. Consequently a polonium hexafluoride, volatile at room temperature, with a heat of formation in the neighborhood of 300,000 calories/mole is indicated.

Leitz and Coulter[14] tried two general methods of preparing a volatile polonium fluoride: (1) metallic polonium was deposited on gold or platinum foils and exposed to fluorine at room temperature and at various temperatures up to 700°C; (2) metallic polonium was mixed with relatively large amounts of selenium or tellurium as carriers and treated with fluorine. Results of these experiments indicated that no volatile fluorides were formed. No systematic attempts were made at Mound Laboratory to prepare nonvolatile polonium fluorides although polonium is known to be quite soluble in hydrofluoric acid. Studies by Wehrmann[15] on the deposition of polonium from hydrofluoric acid showed that solutions containing 2 curies of polonium per milliliter of 1N hydrofluoric acid were unsaturated. No quantitative solubility studies of polonium in hydrofluoric acid have been made at Mound Laboratory.

7. POLONIUM SULFIDE

Polonium is precipitated completely from acidic, basic, or neutral solutions with hydrogen sulfide. The coprecipitation of polonium with the sulfides of lead, bismuth, copper, arsenic, and antimony was reported by the Curies.[16] Although the precipitation of polonium with a sulfide has been widely used, no compounds of polonium sulfide have been separated and characterized. Goode[17] attempted to prepare a compound of polonium and sulfur by heating the elements directly in a quartz capillary tube. Although some unknown lines appeared in the X-ray pattern, it was concluded tentatively that, under the conditions of the experiment, polonium and sulfur did not react. This conclusion was based on the fact that the X-ray pattern for metallic polonium was present in all the preparations, even in the one in which sulfur was known to be present in considerable excess.

8. SOLUBILITY OF POLONIUM COMPOUNDS

8.1 *Solubility of Polonium in Nitric Acid.* A study of the solubility of polonium in nitric acid was made by Orban[18] in 1947. He determined the quantity of polonium which dissolved in nitric acid solutions that varied in acid concentration from approximately 0.1M to nearly 8M and at temperatures of 25, 35, and 45°C. The quantity of polonium which dissolved in nitric acid varied from 4.0 mg/liter at the lowest temperature and acid concentration to 970 mg/liter at the highest temperature and acid concentration.

The solubility experiments were made with purified polonium which was plated on platinum foils, measured in a calorimeter, and then allowed to stand in moist air until the polonium was converted to the oxide. The foils which contained two or three times as much of the oxide as would dissolve were placed in specially designed solubility tubes which contained 1.5 to 2.0 ml of the nitric acid under investigation. The tubes, Fig. 4.10, were equipped with a capillary thermocouple well which contained a drop of mercury to improve heat transference. Constant environmental temperature within 0.1 to 0.3°C was

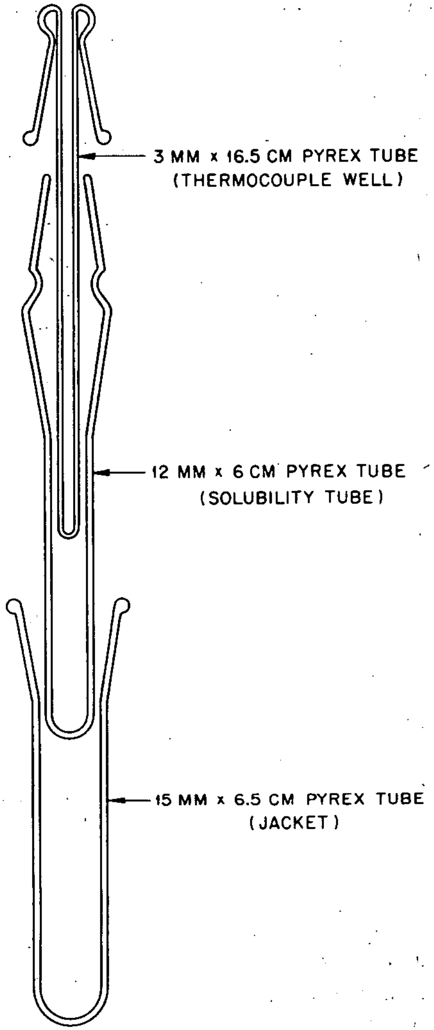


Fig. 4.10 — Solubility tube.

maintained in a dry box for this experiment. The temperature within the solubility tubes was always above that of the air bath by approximately 1°C for each curie of polonium in the tube.

The solutions were centrifuged in the constant-temperature air bath before each measurement of dissolved polonium was made by alpha counting methods. The solutions were sampled in triplicate with calibrated 1- to 10-μl pipettes; then the samples were mounted on glass slides and alpha counted either with a parallel-plate alpha counter or with a Simpson Proportional Alpha Counter. Two 4-min counts were made each day for 20 days on each sample. Background counts were taken twice daily, or more often if contamination of the instrument was suspected. The counts from the triplicate samples of each solution were averaged and corrected for decay to zero time. Since each solution had its own equilibrium temperature because of the varying quantities of total polonium in the tubes, it was necessary to correct the solubilities to 25, 35, and 45°C by interpolation. The corrected results are recorded in Table 4.5 and are shown graphically in Fig. 4.11.

Table 4.5—Solubility of Polonium in Nitric Acid at 25, 35, and 45°C (from Graphic Data)

Concentration of acid, N	Solubility, moles/liter 25°C	35°C	45°C
0.1036	1.9×10^{-5}	2.7×10^{-5}	3.6×10^{-5}
0.5046	7.2×10^{-5}	7.9×10^{-5}	8.6×10^{-5}
1.006	1.38×10^{-4}	1.59×10^{-4}	1.80×10^{-4}
1.595	3.6×10^{-4}	4.4×10^{-4}	5.3×10^{-4}
2.081	6.2×10^{-4}	7.3×10^{-4}	8.4×10^{-4}
3.96	1.62×10^{-3}	1.85×10^{-3}	2.1×10^{-3}
5.72	2.5×10^{-3}	2.9×10^{-3}	3.3×10^{-3}
7.83	3.7×10^{-3}	4.1×10^{-3}	4.6×10^{-3}

The solubility approached an equilibrium value in about 2 days and then appeared to decrease slowly with time. In the higher acid concentrations the apparent decrease in solubility was larger than could reasonably be explained by adsorption on glass, coagulation of radiocolloids, or decomposition of the solvent.

The solubility measurements are estimated as accurate within ±10 per cent in the lower concentrations and within ±5 per cent in the upper half of the concentration range.

An inflection in the solubility curve between 1.1N and 1.2N nitric acid may be assumed to indicate either (1) a change in the oxidation state of the polonium or (2) a change in the composition of the polonium ions in solution. The first assumption appears unlikely since polarographic studies[19] indicate that polonium is oxidized to the tetravalent state in nitric acid concentrations between 0.3N and 0.5N. It seems probable, therefore, that the inflection in the curve results from the

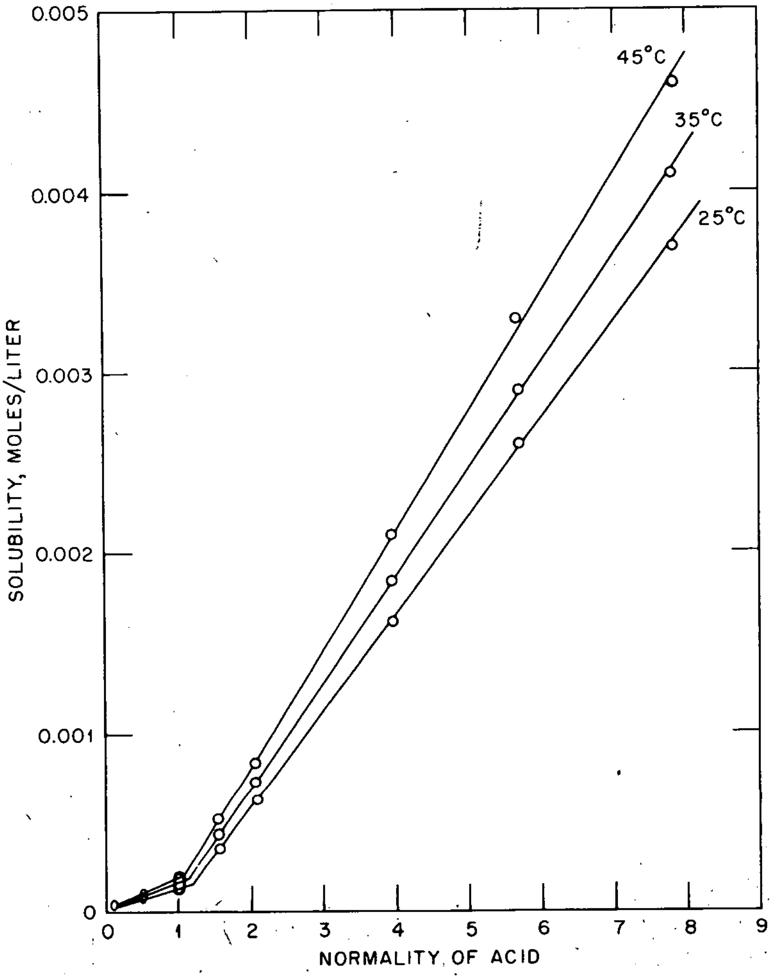


Fig. 4.11—Solubility of polonium nitrate in nitric acid.

formation of a complex anion containing an increased number of nitrate ions. Haissinsky[20] has reported that polonium begins to migrate toward the anode in nitric acid concentrations above 0.1N. This observation has been confirmed at Mound Laboratory by Fainberg, Barth, and Staniforth.[21] Orban[18] suggested that the following equations may indicate the reactions of polonium in nitric acid solutions: below 1.1N nitric acid (Eq. 4.1) and above 1.2N nitric acid (Eq. 4.2).

$$PoO(NO_3)_2 + HNO_3 \rightleftharpoons H^+ + PoO(NO_3)_3^- \qquad (4.1)$$

$$Po(NO_3)_4 + HNO_3 \rightleftharpoons H^+ + Po(NO_3)_5^- \qquad (4.2)$$

No systematic studies of the solubility of polonium in acids other than nitric acid have been made at Mound Laboratory. However, observations by various workers have produced some qualitative information.

8.2 *Hydrochloric Acid.* The solubility of polonium is high in hydrochloric acid in comparison with its solubility in other solvents. Schulte[22] prepared an unsaturated solution of polonium in 0.5N hydrochloric acid in which 8.95 curies of polonium per milliliter of solution were dissolved. Concentrated solutions of polonium in hydrochloric acid are yellow in color, probably as a result of the formation of complex ions which may have the composition $PoCl_6^{--}$. Schulte also observed that 1 curie of polonium chloride does not dissolve completely in 5 ml of 0.1N hydrochloric acid, although the same quantity of polonium is easily dissolved in 5 ml of 0.2N hydrochloric acid. If the 0.1N acid is made 5N in ammonium chloride, the polonium chloride dissolves as would be expected if a complex polonium chloride ion is formed. Light-transmission studies[22] on hydrochloric acid solutions of polonium indicate that 1 curie of polonium in 5 ml of solution is completely converted to the yellow polonium chloride complex when the acid concentration reaches 0.5N.

8.3 *Sulfuric Acid.* Schulte[22] concluded that the solubility of polonium in 1N sulfuric acid is less than 0.05 curie/ml. Harlow,[23] from observations made at Los Alamos Scientific Laboratory, reported the solubility of oxidized polonium as 2.3 mc/ml in 0.1N sulfuric acid.

8.4 *Hydrofluoric Acid.* Polonium is readily soluble in hydrofluoric acid solutions. Wehrmann[15] studied the electrodeposition of polonium from hydrofluoric acid solutions. He prepared unsaturated solutions containing 2 curies of polonium per milliliter in molar hydrofluoric acid. The high solubility suggests the formation of polonium fluoride complex ions.

8.5 *Phosphoric Acid.* The solubility of polonium in phosphoric acid is low. Schulte[22] observed that at least 10 ml of 4M phosphoric acid was required to dissolve 2 curies of polonium. He reported the formation of a gelatinous precipitate when 10 ml of phosphoric acid below 4N was added to 2 curies of polonium nitrate or chloride.

8.6 *Perchloric Acid.* The solubility of polonium in perchloric acid is similar to its solubility in sulfuric acid. Wehrmann[15] reported the preparation of a perchloric acid solution of polonium in which 1M perchloric acid was added to the residue obtained by evaporating a nitric acid solution of polonium. He succeeded in dissolving approximately 1 curie of polonium nitrate in 8 ml of molar perchloric acid; however, when a second curie of polonium nitrate was added and the solution was evaporated to remove nitrate ions, a gelatinous white precipitate formed which did not redissolve upon dilution to the original volume with molar perchloric acid.

8.7 *Citric, Oxalic, Tartaric, and Acetic Acids.* A number of observations have been made which suggest the probability that polonium forms complex ions with citric, oxalic, and tartaric ions (see Chap. 6, Table 6.6). Schulte,[22] in his studies on the electrodeposition of polonium from various solvents, observed that the addition of these acids increased the solubility of polonium in phosphoric acid. Citric and oxalic acids were more effective in this respect than tartaric acid. No quantitative measurements of the solubility of polonium in aqueous solutions of citric, oxalic, and tartaric acids have been made at Mound Laboratory. Unsaturated solutions of polonium have been prepared by Schulte in which 1.5 curies of polonium chloride dissolved in 10 ml of 0.05M citric acid. He also prepared unsaturated solutions of polonium nitrate containing 0.075 curie of polonium, respectively, in 10 ml of 0.1M, 0.5M, and 1.0M solutions of oxalic acid. However, solutions of 0.5M tartaric acid containing 0.37 curie of polonium in 10 ml were unstable; a dark precipitate formed on standing which carried down the activity.

Schulte[22] reported the preparation of unsaturated solutions of polonium in 50 per cent acetic acid which contained 1 curie of polonium in 10 ml of solution.

8.8 *Sodium Hydroxide.* Several experiments were made by Haring[24] to determine the solubility of the hydrous oxide of polonium in 1.5N sodium hydroxide. He treated 1.57 curies of polonium, which was mounted on a platinum foil, with 2 ml of 1.5N sodium hydroxide. Immediately the polonium oxide swelled and detached itself from the foil. The tube and contents were agitated frequently for about 4 hr at room temperature and then heated nearly to boiling under an infrared lamp for approximately 4 hr. The tube was shaken occasionally during the heating. Nearly all the residue dissolved. The tube was allowed to stand for 1 week and was subjected daily to a vigorous shaking. After a second week of standing, a gray residue settled in the tube. Samples of the supernatant solution were carefully removed, in order not to disturb the precipitate, and alpha counted. The concentration of polonium was found to be 2.8×10^{-4}M (0.27 curie/ml) at approximately 25°C. Two other experiments, less carefully carried out, gave 0.31 and 0.43 curie/ml, respectively.

Experiments were made at the Los Alamos Scientific Laboratory, as reported by Harlow,[23] in which the rate of solubility of polonium in 1.5N sodium hydroxide was determined. Polonium was plated on platinum foils and allowed to oxidize in air for several days. The foils were then placed in glass tubes containing a measured volume of 1.5N carbonate-free sodium hydroxide and kept agitated in a constant-temperature bath held at 25 ± 0.1°C. After various intervals of time, the solutions were assayed by alpha counting to determine the rate at which the polonium dissolved. Each solution was centrifuged before counting. The procedure followed in these experiments differs from that used by Haring in that a temperature of 25°C was maintained throughout the tests, whereas Haring heated his solutions almost to boiling for 4 hr before allowing them to stand. The results of the experiments reported by Harlow show that about 50 per cent of the maximum solubility is reached in 1 hr and that the maximum concentration is reached in 21 to 46 hr. Harlow reported a solubility of 0.100 to 0.105 curie/ml or roughly one-third of the values reported by Haring.

8.9 *Solubility of Polonium Oxide in Various Reagents.* A number of experiments were made at the Los Alamos Scientific Laboratory and reported by Harlow[23] in which oxidized polonium on platinum foils was placed in aqueous solutions of various reagents and the solubility measured in the same apparatus as was used to determine the rate of solubility in sodium hydroxide. The results are shown in Table 4.6.

Several differences may be observed between the results reported in Table 4.6 and the qualitative observations made at Mound Laboratory. This may be accounted for, in part at least, by the tendency of polonium to form colloidal dispersions in weakly acidic or weakly basic solutions.

9. COLLOIDAL PROPERTIES OF POLONIUM

9.1 *Introduction.* The tendency of polonium to form colloidal solutions has long been recognized,[25] but the literature on the subject is scanty and confusing. Fainberg and coworkers[26] studied the colloidal properties of polonium through experiments involving the dialysis of solutions of polonium and the rates of settling of insoluble polonium compounds, over a wide range of pH values. The experiments were designed to determine whether the amphoteric character of polonium would lead to the formation of precipitates of colloidal dimensions as the pH was varied from acidic to neutral to basic values. Sedimentation studies were made to differentiate between coarse dispersion and colloidal or ionic dispersion.[27]

9.2 *Experimental Methods.* The purpose of these studies was to determine the percentage of polonium in solutions at various pH values

Table 4.6—Solubility of Oxidized Polonium

Solution Used	Formula	Concentration, M	Solubility, mc/ml
Sodium nitrate	$NaNO_3$	1.5	1.4
Sodium carbonate	Na_2CO_3	0.5	1.4
Sodium carbonate	Na_2CO_3	0.05	1.6
Ammonium carbonate	$(NH_4)_2CO_3$	0.75	24.0
Ammonium carbonate	$(NH_4)_2CO_3$	0.25	0.4
Ammonium hydroxide	NH_4OH	18	1.0
Sulfuric acid	H_2SO_4	0.05	2.3
Orthophosphoric acid	H_3PO_4	0.5	30.0
Potassium dihydrogen orthophosphate	KH_2PO_4	1.0	4.0
Ammonium monohydrogen orthophosphate	$(NH_4)_2HPO_4$	1.0	1.7
Sodium monohydrogen orthophosphate	Na_2HPO_4	1.0	4.8
Acetic acid	CH_3COOH	1.0	128
Sodium acetate	CH_3COONa	1.0	0
Oxalic acid	$H_2C_2O_4$	0.5	42
Potassium oxalate acid	HKC_2O_4	0.4	62
Citric acid	$(COOH)CH_2C(OH)-(COOH)CH_2COOH$	1.0	46
Potassium cyanide	KCN	1.0	3.8
Potassium acid tartrate	$KHC_4H_4O_6$	1.0	41

which was dialyzable, the percentage which was nondialyzable, and the percentage which settled out or adsorbed on the walls of the container.

The polonium used in the experiments was purified by volatilization from platinum foils into clean quartz tubes from which it was dissolved in 1.5N nitric acid. Solutions at each pH value were divided into two parts, designated A and B. The two solutions were identical in every respect except that polonium was added to solution A and omitted from solution B. Solution A was treated with enough sodium hydroxide to neutralize the nitric acid which accompanied the polonium, and an equivalent amount of sodium nitrate was added to solution B. The dialyzing membranes were prepared from Baker's U.S.P. collodion. Test tubes 13 mm in diameter by 100 mm long were used as forms. The membranes required for each set of experiments were prepared at the same time from fresh collodion. An identical procedure was used in preparing the collodion bags in order to ensure uniformity in the membranes. From 2 to 4 ml of collodion was poured into a test tube which was rotated and inverted in order to coat the inside of the test tube. The tube was held upside down, tipped slightly, and then slowly rotated as the collodion drained out. The tube was allowed to dry for 15 min in an inverted position, and then the excess collodion was trimmed from the top with a razor blade. The tube was filled with distilled water and allowed to stand for at least 4 min. It was found that collodion bags could be kept for several hours in this condition with no apparent change.

When the membranes were ready to use, the distilled water in the bag was poured out and 10 sec was allowed for drainage. Two milliliters of the active solution was introduced, and the collodion bag was withdrawn from the test tube and placed into 5 ml of inactive solution B. The inactive solutions were placed in short test tubes, 54 mm long by 15 mm in diameter, which were held upright in holes in a wooden block. The membrane containing 2 ml of solution A was lowered carefully into the 5 ml of solution B until the level of liquid inside the bag was the same as that outside, and then the upper portion of the bag was folded over the edge of the test tube. After 15 min the bag was raised partially from the solution and then lowered to the original level. This was repeated several times in order that the more concentrated layer of material on the outside of the bag was left in solution B. The bag was then removed and its contents discarded. Solution B was thoroughly stirred and analyzed for polonium. The 15-min period of time for a given dialysis experiment was selected because a series of experiments with nitric acid solutions of polonium showed that dialysis averaged 32 per cent of completion in 15 min, and the results were reproducible within ±5 per cent. Figure 4.12 shows the per cent of theoretical equilibrium plotted against time. Each point on the curve

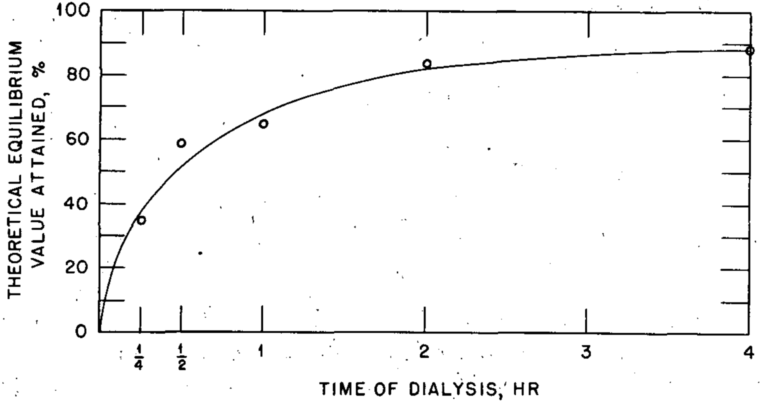


Fig. 4.12—Dialysis of polonium–nitric acid solutions.

is the average of 6 to 12 experiments at the given time with nitric acid solutions in which the polonium was assumed to be completely dialyzable. The temperature of the experiments varied from 24 to 26°C. The polonium content of the initial solutions used to determine the rate of dialysis varied from 2.5×10^7 dis/min/ml to 3.7×10^9 dis/min/ml or approximately 0.012 to 1.7 mc/ml. The percentage dialyzable was independent of concentration within the limits of error in the measurements. Since there were 2 ml of solution A and 5 ml of solution B, equilibrium would be reached when each milliliter of B contained $^2/_7$ of the original concentration in solution A. The percentage of dialyzable polonium in a solution was calculated as follows:

$$\text{Per cent dialyzable} = \frac{\text{concentration of polonium in B}}{^2/_7 \text{ concentration in A}} \times \frac{100}{0.32}$$

9.3 *Dialysis of Polonium in Buffered Solutions.* Three sets of solutions, R, S, and T, were prepared, each set consisting of 15 solutions of pH 0 to 15 in steps of 1 pH unit. The A solutions of these sets contained the following concentrations of polonium:

Set R, 2.3×10^9 dis/min/ml or 1.04 mc/ml
Set S, 2.5×10^8 dis/min/ml or 0.113 mc/ml
Set T, 2.6×10^7 dis/min/ml or 0.0117 mc/ml

After the solutions were prepared, they were allowed to stand 2 to 4 days; then they were shaken thoroughly and dialyzed. The portions of these solutions remaining after the dialysis experiments were completed were allowed to stand for 73 days, during which time sedimentation studies were made.

The results of the dialysis experiments on polonium solutions at different pH values are shown graphically in Fig. 4.13. The increase in dialyzable polonium at pH 7 and 8 was suggested by Fainberg and coworkers[26] as possibly due to the formation of complex ions with the buffering salts, particularly the primary and secondary phosphates which were used to buffer the solutions at pH 7 and 8.

In order to test the effect of different buffering substances, Fainberg and Barth prepared 30 buffer solutions ranging in pH from 1.9 to 13. Clark and Lubs' and Sorenson's buffers were prepared according to the procedure outlined by Clark.[28] The various buffers contained citrates, phthalates, phosphates, borates, and glycine. Citrates appeared to form complex ions from pH 2 to 6. Phthalates formed complex ions, but less strongly than citrates, between pH 3 and 6. Phosphates did not complex up to pH 6 but combined to a small extent at pH 8. Borates and glycine showed no evidence of complex formation with polonium.

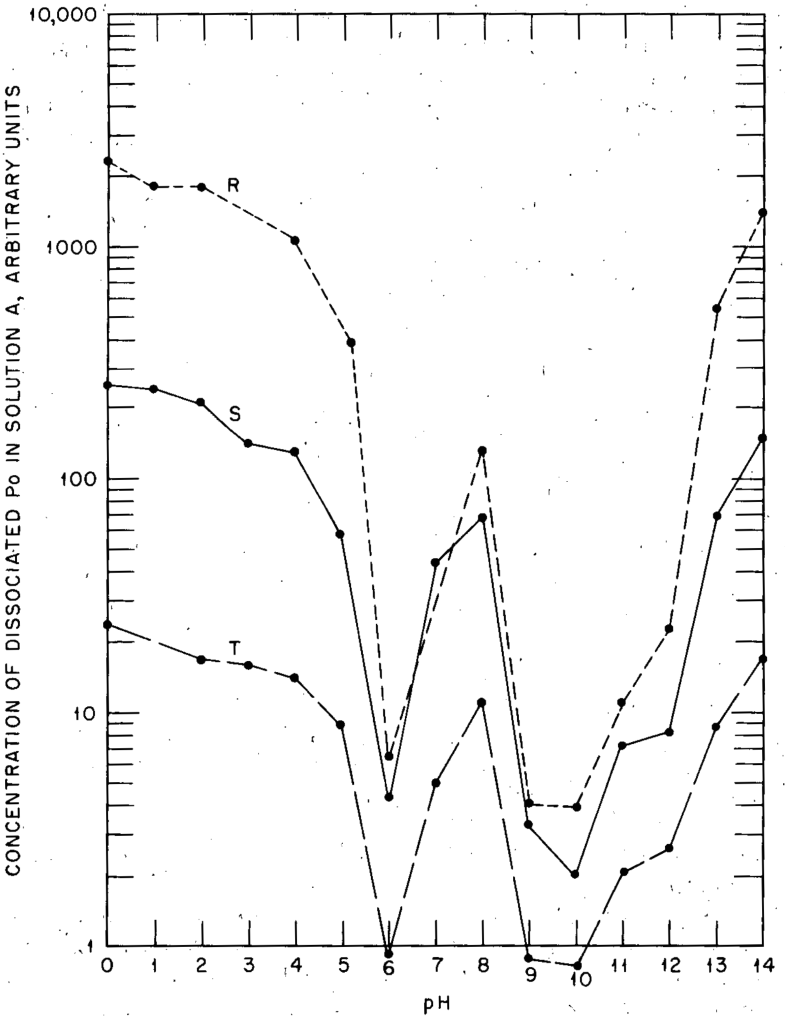


Fig. 4.13—Dialysis of polonium in 1.5N nitric acid. R, 2.3 × 10^9 dis/min/ml. S, 2.5 × 10^8 dis/min ml. T, 2.6 × 10^7 dis/min/ml.

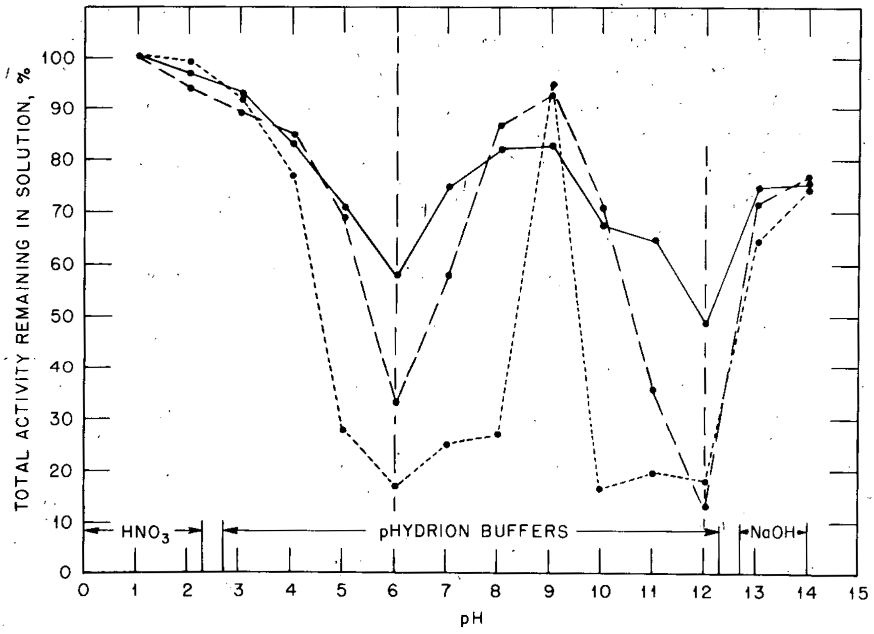
9.4 *Dialysis of Unbuffered Polonium Solutions.* The increase in the per cent of polonium which passed through the collodion membrane in the neutral pH range, as indicated in Fig. 4.13, suggested the desirability of studying the dialysis of polonium in unbuffered solutions. A series of experiments was made by Barth and Power[29–32] in which unbuffered solutions from pH 3 to 9 were dialyzed. They modified the conditions of dialysis as described by Fainberg and coworkers[26] by allowing the dialysis to continue for 24 hr instead of for 15 min. They found that solutions of polonium in 1.5N nitric acid reached 93 per cent of the theoretical equilibrium value in 24 hr. The unbuffered solutions were prepared by adding the purified polonium in 1.5N nitric acid to distilled water placed in a polystyrene container. The nitric acid was titrated with sodium hydroxide solution until the desired pH was reached as shown by a Beckman glass electrode. Nitrogen gas was bubbled through the solution for 15 min before the pH readings were taken. They used collodion membranes which were prepared as described by Fainberg and coworkers.[26] The concentrations of polonium in the A solutions varied from 1.06×10^8 to 3.0×10^8 dis/min/ml. These concentrations were roughly the same concentration as for the S solution indicated in Fig. 4.13. The results are shown in Table 4.7 and indicate that, with buffering salts absent, polonium does not redisperse into dialyzable forms in the neutral pH range.

Table 4.7—Dialysis of Unbuffered Solutions at 25°C for 24 Hr

No. of runs	Measured pH of solution A	Measured pH of solution B	Initial concentration of solution A, mc/ml	% dialyzable	Probable error of mean
5	3.04	3.03	0.38	50	±1.1
8	4.02	4.01	0.18	9.2	±0.2
6	4.98	4.95	0.49	1.7	±0.5
7	6.02	5.99	0.47	0.8	±0.1
6	6.98	6.99	0.50	0.4	±0.1
7	8.11	8.20	0.40	0.44	±0.03
5	8.95	8.98	0.44	0.62	±0.08

9.5 *Sedimentation Studies.* The three sets of solutions, R, S, and T, which are described in Sec. 9.3, were used also in sedimentation studies. After samples had been withdrawn for dialysis, the solutions were allowed to stand undisturbed for varying periods of time. Samples for analysis were withdrawn from the upper ¼ in. of solution. After a sample of the undisturbed solution was analyzed, the solution was shaken and an analysis was made of the agitated solution. Results of sedimentation measurements on the three sets of solutions are shown in Fig. 4.14. The effect of shaking is shown in Figs. 4.15 to 4.17.

9.6 *Discussion of Dialysis and Sedimentation Studies.* The per cent of theoretical dialysis equilibrium was approached to between 90 and



	Po concentration, dis/min/ml	Settling time, hr
——,	2.6×10^{7} (T)	72
– – –,	2.5×10^{8} (S)	120
- - - -,	2.3×10^{9} (R)	60

Fig. 4.14—Sedimentation studies on R, S, and T solutions.

100 per cent, as shown in Fig. 4.12, as the experimentation time was prolonged indefinitely. These observations were made with collodion membranes and indicate that no significant amount of polonium was adsorbed on the collodion. This is in contrast with results obtained by Barth and Power,[29–32] who studied dialysis through Visking (Visking Corp., Chicago, Ill.) sausage cellulose casing membranes. They found that a fresh membrane removed nearly all the activity from hydrochloric or nitric acid solutions of polonium. After saturation with polonium, these membranes appeared to be more desirable than collodion for dialysis studies because they had a smaller pore size. However, the dialysis experiments of Fainberg and coworkers[26] were not repeated with the cellulose membranes.

The results of the dialysis and sedimentation studies are expressed

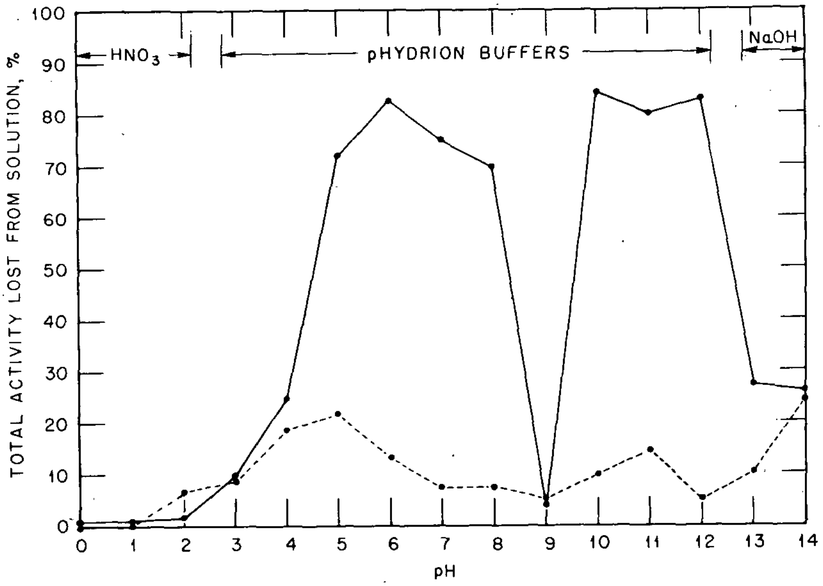


Fig. 4.15—Loss of polonium from solution; solution R. 2.3 × 10^9 dis/min/ml. After 60 hr standing: ——, before shaking; ----, after shaking.

in per cent of the total polonium activity at a given time; hence the radioactive decay of the polonium is eliminated in comparing results at different times.

Dialysis and sedimentation studies indicate that polonium in solution at different pH values distributes itself as follows: (1) some exists as ions, either simple or complex; (2) some forms colloidal particles; (3) some settles out as insoluble particles; and (4) some is adsorbed on the walls of the container. Polonium is largely ionic in the pH ranges 0 to 3 and 13 to 14. It forms an insoluble compound in solutions of pH 4 to 12. Polonium exhibits a minimum solubility near pH 6 and again between pH 9 and 12.

A stable colloid was formed only at pH 9 in all three solutions. At this pH no appreciable settling in any solution occurred in 30 days. After 70 days nearly all the polonium had settled in all the solutions.

Radiocolloidal effects are not indicated as a major factor in the sedimentation data since a larger percentage of the total polonium settled out at a given pH in the most concentrated of the three solutions.

There is evidence of the formation of an insoluble phase in the pH range between 6 and 10 since the total ionic polonium content in all

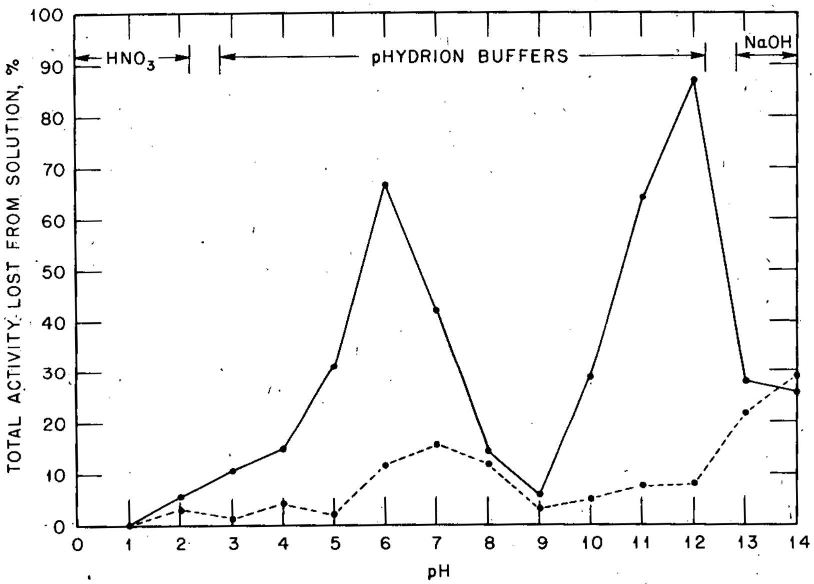


Fig. 4.16—Loss of polonium from solution; solution S. 2.5 × 10^8 dis/min/ml. After 120 hr standing: ——, before shaking; ----, after shaking.

three solutions was shown by dialysis to be practically the same even though the ratio of concentrations of polonium in the starting solutions was close to 100:10:1. This would be predicted from solubility product relations since the precipitating ion was constant at the same pH in each of the three solutions.

The experiments at Mound Laboratory confirm the observations of a number of early workers[33–36] that polonium exists as ions in strongly acid and strongly basic solutions but behaves as a colloid in weakly acid, neutral, and slightly basic solutions.

10. COMPLEX IONS OF POLONIUM

10.1 *Cataphoresis Experiments.* It is generally assumed that the high solubility of polonium in certain acid solutions, notably hydrochloric, hydrofluoric, oxalic, and citric, is due to the formation of complex ions. Staniforth and Barth,[37–42] in cataphoresis experiments, showed that polonium forms both cations and anions in nitric and sulfuric acids as well as in hydrochloric acid. Equal concentrations of anions and cations were observed in approximately 0.05N solutions of

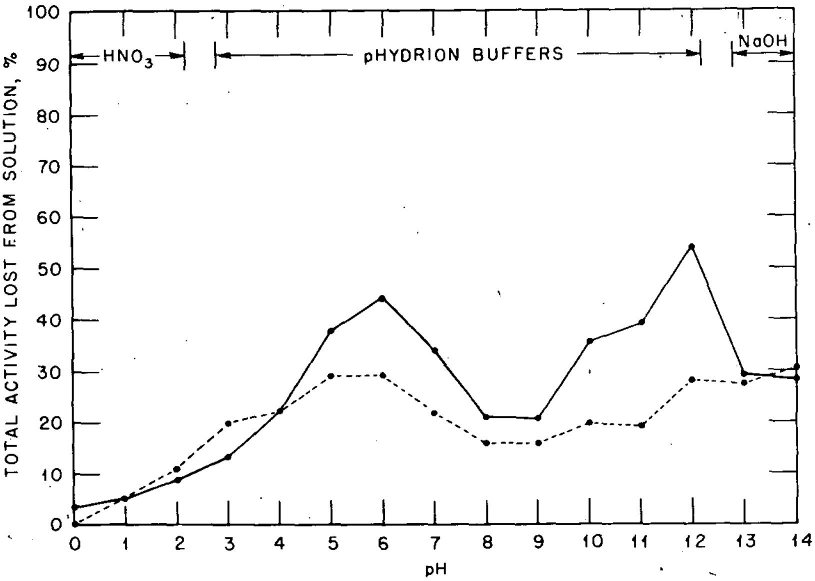


Fig. 4.17—Loss of polonium from solution; solution T. 2.6 × 10^7 dis/min/ml. After 72 hr standing: ——, before shaking; ----, after shaking.

any one of the three acids. The cataphoresis experiments gave qualitative evidence that in acid solutions, 0.5N or above, polonium is present almost completely in the form of ions which migrate toward the anode. In weakly acid and neutral solutions, polonium exhibits a greater tendency, under the applied potential, to migrate toward the cathode. However, the movement of the activity toward the cathode in nearly neutral solutions may be the result of migration of charged colloidal particles since dialysis experiments indicate particle formation between pH 4 and 9. Results of cataphoresis experiments by Staniforth and Barth are in good agreement with results reported by Samartseva,[25] except in the case of sulfuric acid solutions of polonium. Samartseva reported greater migration toward the cathode in 0.1N to 5.0N sulfuric acid. Staniforth and Barth found that, in sulfuric acid solutions 0.1N and above, migration of polonium is predominantly toward the anode.

10.2 *Absorption Spectra Studies of Polonium Chloride Solutions.* (a) *Introduction.* Preliminary studies of polonium complex-ion formation in hydrochloric acid were made at Mound Laboratory by McCluggage.[43] He obtained an absorption spectrum for 0.94 × 10^{-5}M polonium in 4.757N hydrochloric acid. He also observed an absorption peak close to 420 mμ and strong absorption at approximately 260 mμ. Studies reported elsewhere[44,45] on 1.9×10^{-6}M polonium in 0.5M hydrochloric acid show a rather narrow absorption band with a maximum at 415 mμ. These workers[44,45] suggest the formation of $PoCl_6^{--}$ as a probable complex ion since salts containing this anion have been precipitated from strong hydrochloric acid solutions. An absorption maximum at a wavelength of 345 mμ was also reported.[45]

Hunt[46] continued the study, at Mound Laboratory, of the absorption spectra of polonium in hydrochloric acid solutions.

(b) *Experimental Technique.* Hunt used a Cary Recording Spectrophotometer to record the absorption spectra of polonium over the entire range of the instrument, 220 to 795 mμ. The active solutions contained approximately 0.02 to 0.2 curie of polonium per milliliter and were handled according to the technique devised by McCluggage.[43] The active solutions were transferred in a closed hood to the absorption cells by means of a medical syringe attached to a glass tube, which was drawn down to capillary dimensions at the end which was placed in the solutions. One-centimeter quartz absorption cells were used. They were sealed with sheet paraffin with the aid of an infrared lamp and a glass rod. The cells were then transferred in a holder to another hood where they were wiped with dilute hydrochloric acid until they were "wipe-free" of activity. Practically no contamination of the instrument resulted from solutions handled in this manner.

(c) *Theory.* Hunt investigated the equilibrium between the complex ions of polonium which are responsible for the respective absorption maxima at 344 and 418 mμ. He used an adaptation of the theoretical approach suggested by Bent and French.[47] If the following reaction is assumed:

$$\mathrm{mA} + \mathrm{nB} \rightleftharpoons \mathrm{A_m B_n} \tag{4.3}$$

the equilibrium constant is

$$K = \frac{[\mathrm{A_m B_n}]}{[\mathrm{A}]^m [\mathrm{B}]^n} \tag{4.4}$$

whence

$$\log [\mathrm{A_m B_n}] = m \log [\mathrm{A}] + n \log [\mathrm{B}] + \log K \tag{4.5}$$

If $A_{[A_m B_n]}$ represents the absorbancy due to $[A_m B_n]$, from Beer's law,[48]

$$A_{[A_mB_n]} = ab\,[A_mB_n] \tag{4.6}$$

where a is the absorbancy index and b is the cell thickness. Then

$$\log\,[A_mB_n] = \log A_{[A_mB_n]} - \log ab \tag{4.7}$$

Substitution in Eq. 4.5 gives

$$\log A_{[A_mB_n]} = m \log\,[A] + n \log\,[B] + C \tag{4.8}$$

in which C is a constant equal to log K + log ab.

If the absorbancy of the complex, $\log A_{[A_mB_n]}$, is plotted against the logarithm of the concentration at equilibrium of one of the reactants with the concentration of the other reactant held constant, a straight line should result, the slope of which is equal to the number of moles, m or n, of the reactant in the complex.

(d) *Preliminary Experiments.* Hunt found that 0.01M calcium hypochlorite in 1M hydrochloric acid showed absorption peaks, due to free chlorine, at 230 mμ and at about 335 mμ. Since free chlorine is always present in hydrochloric acid solutions of polonium, as a result of alpha bombardment, he concluded that most of the absorption below 375 mμ is due to chlorine and that reliable quantitative data would be more difficult to obtain in this region. The peak close to 420 mμ was not present in the calcium hypochlorite–hydrochloric acid solutions. Preliminary studies showed a difference in the absorption spectra of polonium in 0.1M and 1M hydrochloric acid. In Fig. 4.18 the absorbancy curves for polonium in 0.12M and 1.2M hydrochloric acid solutions are shown. Both curves show absorption in the ultraviolet region below 350 mμ. Much of this can be attributed to chlorine; however, the stronger acid shows a maximum at 247 mμ and a slight shoulder at 260 mμ superimposed on the chlorine absorption. The peak at 247 mμ did not appear in the 0.12M acid solution although a shoulder appeared at about 260 mμ. The absorption peak at 418 mμ in the stronger acid is not present in the absorption curve of the weaker solution. These results are in general agreement with work done elsewhere.[44,45] The differences in the two curves show that polonium is present in hydrochloric acid solution in at least two different forms. Attention was directed to the 418-mμ maximum since at this wavelength the chlorine interference was absent.

(e) *Absorption Spectra in Strong Hydrochloric Acid.* Experiments with nearly constant-quantity-polonium solutions, approximately 3×10^{-5}M, in 2M, 3M, 4M, and 5M hydrochloric acid showed no appreciable change in absorbancy at 418 mμ. The molar absorbing index at this wavelength in the more concentrated acid solutions agreed, within the

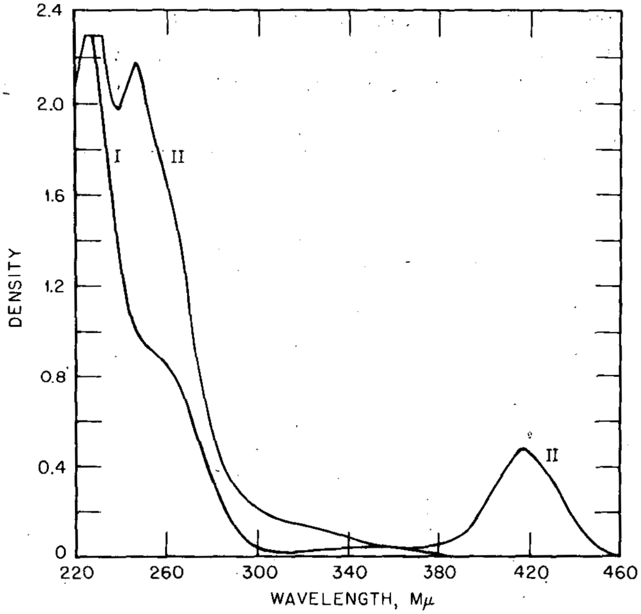


Fig. 4.18—Polonium absorbancy curves. I, 4.5 × 10^{-5}M Po in 0.12M HCl. II, 4.3 × 10^{-5}M Po in 1.2M HCl.

experimental error of alpha counting, with the value found in the 1.2M solution. The complex formation responsible for the 418-mμ absorption peak appears to have reached virtual completion even in 1.2M hydrochloric acid. This conclusion was strengthened by the observation of absorption curves obtained from a series of samples in which the polonium and chloride were kept constant while the hydrogen-ion concentration was varied. A series of six solutions was prepared by diluting 1-ml volumes of a 12.2M hydrochloric acid solution, 6 × 10^{-4}M in polonium, to final volumes of 10 ml by adding varying proportions of 12.2M hydrochloric acid and 12.2M lithium chloride. The six solutions yielded absorbancy indices calculated at the 418-mμ wavelength which were constant among themselves, within the errors of the alpha counting which established the amount of polonium in the solution, and agreed with the values obtained from solutions of polonium in hydrochloric acid alone. No new absorption maxima appeared in the more concentrated acid solutions. The results indicated that, in order to shift the equilibrium away from the 418-mμ complex and toward the 344-mμ complex, it would be necessary to use hydrochloric acid solutions between 0.1M and 0.5M.

A careful determination of the absorbancy index at 418 mμ was made in acid solutions in which a higher chloride complex was dominant. The polonium concentrations were determined calorimetrically and corrected for decay to the time the absorption spectra were recorded. The results are shown in Table 4.8, and the calculated absorbancy index is included.

Table 4.8—Absorbancy Index of the Polonium Chloride Complex at 418 mμ

Sample No.	Molarity ($\times 10^{-5}$) of polonium by calorimetry	Absorbancy at 418 mμ	Absorbancy index $\times 10^4$
A	5.425	0.598	1.094
B	5.447	0.585	1.065
C	6.332	0.667	1.045
D	6.069	0.667	1.090
E	3.122	0.338	1.074
F	3.744	0.370	0.980
		Mean value	1.058 ± 0.028

(f) *Absorption Spectra in Dilute Hydrochloric Acid.* Stronger solutions of polonium were needed to obtain reliable data with respect to the 344-mμ absorption peak. The concentration of hydrochloric acid was adjusted to the range from 0.15M to 0.61M since in this range of acid concentration the equilibrium can be shifted appreciably from one complex to the other. Results are shown in Table 4.9. An attempt was made to prepare 0.06M and 0.12M hydrochloric acid solutions which would be 1.2×10^{-4}M and 2.4×10^{-4}M, respectively, in polonium. However, in each solution white precipitates appeared after preparation.

The absorption curve of solution No. 4 of Table 4.9 is shown in Fig. 4.19. The absorbancy at 418 mμ was obtained directly from the curves since there was no interference at this wavelength. However, in order to determine the absorbancy at 344 mμ, the effect of free chlorine had to be subtracted. This was done with the aid of log absorbancy curves.[49] It was assumed that at 418 mμ the effect of chlorine on the polonium absorption curve was negligible and that at 280 mμ the effect of polonium on the chlorine absorption curve was negligible.

An analysis of the data on the assumption that the reaction is Po + $nCl^- \rightleftharpoons PoCl_n$ was made, but it was concluded that the data did not support this assumption.

Table 4.9—Absorbancy at 418 and 344 mμ of Polonium Chloride in Dilute Hydrochloric Acid Solutions

Sample No.	[HCl], M	[Po], M × 10^{-4}	Absorbancy A_{418}	Absorbancy A_{344}	Ratio A_{418}/A_{344}	Log ratio log A_{418}/A_{344}
1	0.610	2.224	2.288			
2	0.488	2.250	2.207	0.021	105.1	2.022
3	0.366	2.234	2.070	0.112	18.5	1.267
4	0.244	2.225	1.570	0.347	4.52	0.655
5	0.610	1.118	1.168			
6	0.304	1.113	0.959	0.117	8.20	0.914
7	0.183	1.107	0.466	0.247	1.89	0.276
8	0.152	0.553	0.137	0.129	1.06	0.025

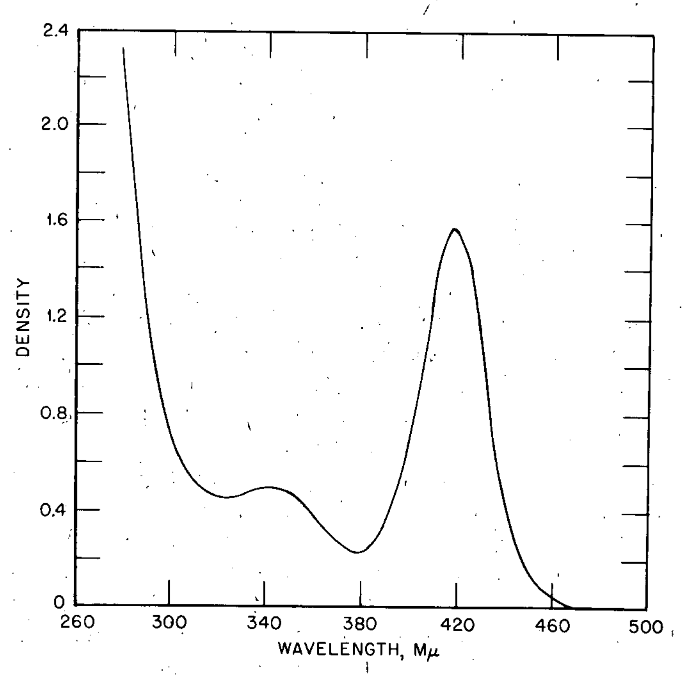


Fig. 4.19—Polonium absorbancy curve in 0.244M HCl. Sample 4: 2.225 × 10^{-4}M Po in 0.244M HCl.

(g) *Effect of Varying pH.* The effect of varying the hydrogen-ion concentration on the absorbancy at 418 and 344 mμ is shown in Table 4.10. The effect of pH is not apparent at higher chloride concentrations but is evident in 0.244M chloride solutions as the hydrogen-ion concentration varied from approximately 0.1M to 0.2M. The solutions were prepared by diluting 1-ml volumes of a solution, 2.2×10^{-4}M in polonium in 0.24M hydrochloric acid, to make equal total volumes but with different proportions of 0.24M hydrochloric acid or 0.24M sodium chloride.

Table 4.10—Absorbancy at 418 and 344 mμ of Polonium Chloride at Varying Concentrations of Hydrogen Ions

Sample No.	$[H^+]$, M	$[Cl^-]$, M	[Po], M × 10^{-4}	Absorbancy A_{418}	Absorbancy A_{344}	Ratio A_{418}/A_{344}	Log A_{418}/A_{344} + log $[OH^-]$
1	0.244	0.244	2.225	1.570	0.347	4.52	−12.729
2	0.195	0.244	0.383	0.262	0.075	3.49	−12.744
3	0.146	0.244	0.383	0.223	0.086	2.59	−12.748
4	0.098	0.244	0.385	0.163	0.098	1.66	−12.768

(h) *Interpretation.* The effect of reducing the hydrogen-ion concentration in 0.244M chloride-ion concentrations caused a lowering in absorbancy at 418 mμ and an increase in absorbancy at 344 mμ. This was interpreted to mean that an increase in the hydroxyl-ion concentration favored the formation of the 344-mμ complex. An attempt was made, therefore, to interpret the data on the assumption that the concentrations of both the hydroxyl ion and the chloride ion were involved in a two-step reaction. The following reactions were assumed:

$$Po + aOH + bCl^- \rightleftharpoons Po(OH)_aCl_b \qquad (4.9)$$

$$Po(OH)_aCl_b + nCl^- \rightleftharpoons PoCl_{n+b} + aOH \qquad (4.10)$$

A partial interpretation of the data is possible since it is possible to evaluate the hydroxyl ion, the chloride ion, and the $PoCl_{n+b}$ concentrations. The hydroxyl-ion concentration is obtained from the known concentration of hydrochloric acid which may be assumed, without appreciable error, to be 100 per cent ionized. The chloride-ion concentration may be assumed to be equal to the added chloride concentration since the quantity of chloride combined with the polonium is a negligible reduction in the total chloride concentration. The $PoCl_{n+b}$ concentration can be calculated from the molar absorbancy index at 418 mμ and the absorbancy at 418 mμ in the particular solution involved. The $Po(OH)_aCl_b$ concentration and the polonium ion cannot be determined individually from these data. The sum of [Po] and $[Po(OH)_aCl_b]$ can be calculated by subtracting the calculated concentration of $PoCl_{n+b}$ from the known polonium concentration in a given solution. The constants n and a in Eqs. 4.9 and 4.10 can be deduced with fair certainty. The equilibrium constant for the reaction indicated in Eq. 4.10 is expressed by

$$K = \frac{[PoCl_{n+b}][OH^-]^a}{[Po(OH)_aCl_b][Cl^-]^n} \qquad (4.11)$$

since $[PoCl_{n+b}] = A_{418}/a_{418}b$, where A_{418} is the absorbancy in the particular sample at 418 mμ, a_{418} is the molar absorbancy index, and b is the cell thickness. Similarly $[Po(OH)_aCl_b] = A_{344}/a_{344}b$.

If these values are substituted in Eq. 4.11 and expressed in logarithmic form,

$$\log c_1 + n \log [Cl^-] = \log \frac{A_{418}}{A_{344}} + a \log [OH^-] \qquad (4.12)$$

where c_1 is a constant equal to $K(a_{418}/a_{344})$.

If the $[Cl^-]$ is held constant as shown in Table 4.10, Eq. 4.12 can be written

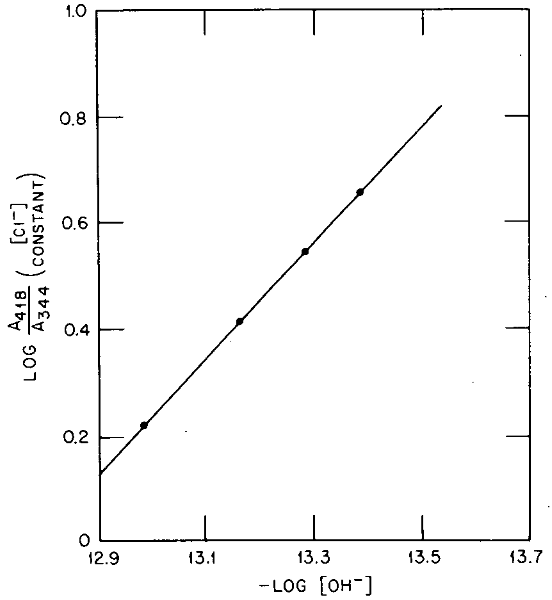
$$\log \frac{A_{418}}{A_{344}} = -a \log [OH^-] + c_2 \qquad (4.13)$$

where $c_2 = \log c_1 + n \log [Cl^-]$.

A plot of $\log A_{418}/A_{344}$ against $-\log [OH^-]$ in Eq. 4.13 should yield a straight line with slope a.

When the data in Table 4.10 are plotted in this manner, a straight line of slope 1.09 is obtained (Fig. 4.20). It was inferred, therefore, that, in Eq. 4.9, a = 1. The correctness of Eq. 4.12 is indicated in Table 4.10 by the constant value for $\log A_{418}/A_{344} + \log [OH^-]$.

The value of n was determined by plotting $\log A_{418}/A_{344} + \log [OH^-]$ against $\log [Cl^-]$ from the data in Table 4.9. The slope, 2.06, is indicated in Fig. 4.21, provided the effects of points 2 and 3 are ignored. The omission of points 2 and 3 is based on the small absorbancy at 344 mμ and the uncertainty in the correction for the effect of free chlorine in 0.366M and 0.488M hydrochloric acid. The points 1, 2, 3, and 4 from solutions of constant chloride concentration (Table 4.10) indicate the constancy of the sum of $\log A_{418}/A_{344} + a \log [OH^-]$ in Eq. 4.12.



$$\text{Slope: } \frac{0.671 - 0.235}{13.4 - 13.0} = \frac{0.436}{0.4} = 1.09$$

Fig. 4.20—Plot of data in Table 4.10 to determine the value of a in Eq. 4.9.

(i) ***Conclusions.*** **The conclusions which can be drawn from the work of Hunt are as follows:**

1. At least two complexes involving polonium and chloride ions exist in hydrochloric acid.

2. If the following equations are assumed,

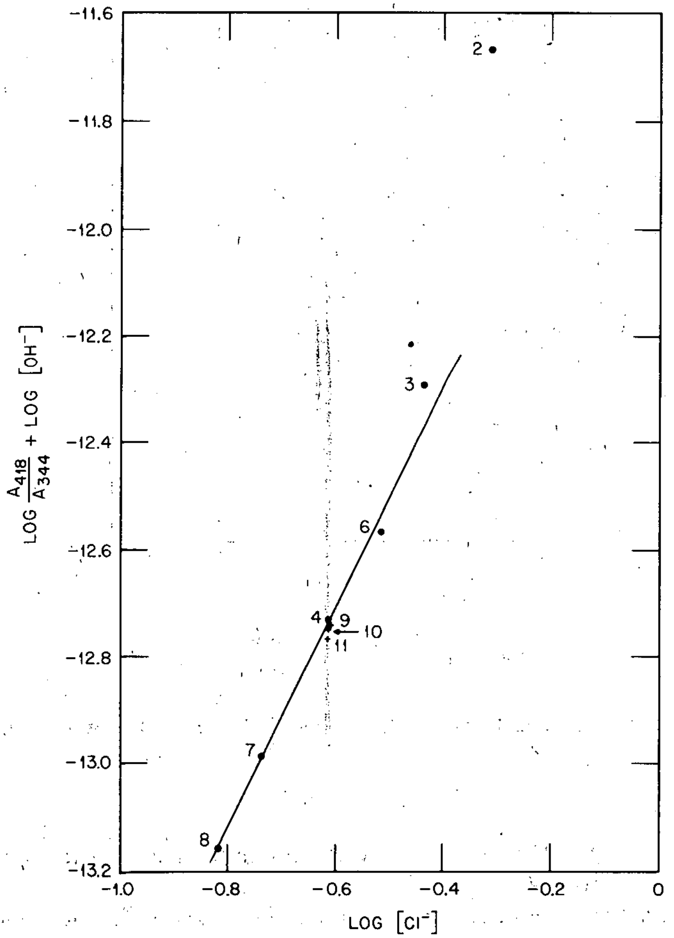
$$Po + aOH^- + bCl^- \rightleftharpoons Po(OH)_aCl_b$$

$$Po(OH)_aCl_b + nCl \rightleftharpoons PoCl_{n+b} + aOH^-$$

the data indicate that a = 1 and n = 2, and that the complex $Po(OH)Cl_b$ is responsible for the absorption peak at 344 mμ, whereas the complex $PoCl_{b+2}$, which is the only one present in hydrochloric acid solutions above 1M, causes the absorption maximum at 418 mμ.

3. The absorbancy index at 418 mμ is 1.06×10^4.

4. The absorption peak at 418 mμ can be used for the colorimetric determination of polonium over a concentration range of 2×10^{-5}M to 2×10^{-4}M in concentrations of hydrochloric acid over 1M.



$$\text{Slope: } \frac{-12.502 - (-13.120)}{-0.5 - (-0.8)} = \frac{0.618}{0.3} = 2.06$$

Fig. 4.21—Plot of data in Table 4.9 to determine the value of n in Eq. 4.10. ●, $[H^+] = [Cl^-]$. +, $[H^+] \neq [Cl^-]$.

11. ELECTROCHEMICAL PROPERTIES OF POLONIUM

11.1 *Introduction.* The early investigations on the electrochemical behavior of polonium are given in Gmelins Handbook[50] and by Haissinsky.[20] Precise values for the standard electrode potential and decomposition potentials in various solvents have not been determined.

There exists, even at present, differences of opinion regarding the possible oxidation states of polonium in solution. Uncertainty arises in determining the electrochemical constants for polonium because of the necessity of working with very dilute solutions of polonium and because of the presence of decomposition products which arise as a result of the alpha bombardment of the solvent.

The spontaneous deposition of polonium on less noble metals is well known. Nickel, copper, bismuth, and silver were used extensively in the isolation of the element by early workers.[50] Under proper conditions polonium will deposit from solution even on the more noble metals, platinum (see references 51 and 52), palladium (see reference 53), and gold (see reference 54). Precipitations on platinum, palladium, and gold are not spontaneous, however, but arise from reduction reactions with hydrogen or other reducing agents.

The tendency of polonium to form complex ions in acid solutions complicates the problem of interpreting data which are taken in attempts to determine decomposition potentials of polonium solutions or to establish standard redox potentials.

11.2 *Electrolysis of Polonium Solutions.*[22] Nitric acid solutions, 1.5N, are quite satisfactory for the electrolytic preparation of polonium metal. The plating solution should be free of gold, platinum, silver, and mercury. Deposits of good quality up to 3 curies/sq cm can be plated on platinum or gold, at room temperature, by using a controlled cathode potential maintained at 0.0 volt with respect to the normal calomel electrode. Approximately 85 per cent of the polonium is deposited at the cathode under these conditions in about 6 hr. Nearly double this time is required to remove 99 per cent of the polonium. No appreciable deposition of polonium occurs at the anode from nitric acid solution. This fact contradicts the observations of early workers[20] who worked with very dilute solutions.

Polonium can be deposited from hydrochloric acid solutions. However, a serious disadvantage is the dissolution of the platinum anode with the subsequent contamination of the polonium with platinum deposited at the cathode. Excellent polonium deposits can be obtained from 1N solutions of hydrofluoric acid. Phosphoric, sulfuric, or perchloric acids are less satisfactory as electrodeposition media because of the low solubility of polonium in solutions of these acids. A considerably more negative cathode potential is required for the electrodeposition of polonium from solutions of oxalic, tartaric, or acetic acid. Nodular, nonadherent deposits from these acids were reported by Schulte[22] as a result of the higher current densities employed. Plating from alkaline solutions is possible, but Schulte reported slow plating from 1.5N sodium hydroxide and difficulty in preparing the solution because of the low solubility of polonium in the alkaline solution.

Schulte[22] reported the results of varying the concentration of nitric acid on the electrolysis of polonium solutions. He found that the rate of deposition decreased in nitric acid concentrations above 1.5N. In 4.0N nitric acid, the rate of deposition was reduced to approximately one-half the rate in 1.5N acid. In 7.5N nitric acid no polonium plated from the solution in 6½ hr.

Schulte[22] reported that current densities less than 4 ma/sq cm in 1.5N nitric acid are more favorable for obtaining uniform polonium deposits. Room temperature is preferred to elevated temperatures. More adherent deposits were obtained on platinum surfaces which had been etched in aqua regia prior to plating. No improvement in the quality of the deposit of polonium was apparent when various wetting agents, beta-naphthalene-sulfonic acid, glycerine, monoethanolamine, and pyridine were added.

11.3 *Decomposition Potentials of Acid Solutions of Polonium.* (a) *Introduction.* Polarographic studies of polonium solutions were made at Mound Laboratory by Haring[55] and Power.[56,57] Haring used platinum electrodes and determined the difference in potential between the platinum cathode and a saturated calomel electrode. The microcell used by Haring is shown in Fig. 4.22. Power used a modification of the Joliot apparatus[58] for measuring the ionization current obtained from the passage of alpha particles through a cathode of gold or platinum foil. The cell used by Power is shown in Fig. 9.31.

(b) *Nitric Acid Solutions of Polonium.* Haring measured the decomposition potential, at 25°C, of 4.44×10^{-4}M and 4.44×10^{-5}M solutions of polonium in 1.5N nitric acid. From an average of eight determinations in each solution, he calculated that the decomposition potential of a 10^{-3}M solution of polonium in 1.5N nitric acid is $+0.332 \pm 0.012$ volt referred to the saturated calomel electrode provided an oxidation change of 2 is assumed. If an oxidation change of 4 is assumed, the decomposition potential of a 10^{-3}M polonium solution is $+0.320 \pm 0.013$ volt in 1.5N nitric acid. Typical curves from Haring's work are shown in Figs. 4.23 and 4.24.

The value reported by Haring is approximately 0.2 volt less positive than the decomposition potential measured by early workers[20] in 0.1N nitric acid solutions which were 10^{-10}M to 10^{-8}M in polonium. The data from which Haring made his calculations of decomposition potentials are shown in Table 4.11.

Haring concluded that his data suggested an oxidation state of +2 for polonium in nitric acid, although the evidence was not conclusive.

(c) *Hydrochloric Acid Solutions of Polonium.* Haring[55] found that the decomposition potential of 10^{-3}M polonium in 1.5N hydrochloric acid at 25°C is $+0.494 \pm 0.012$ volt referred to the saturated calomel electrode.

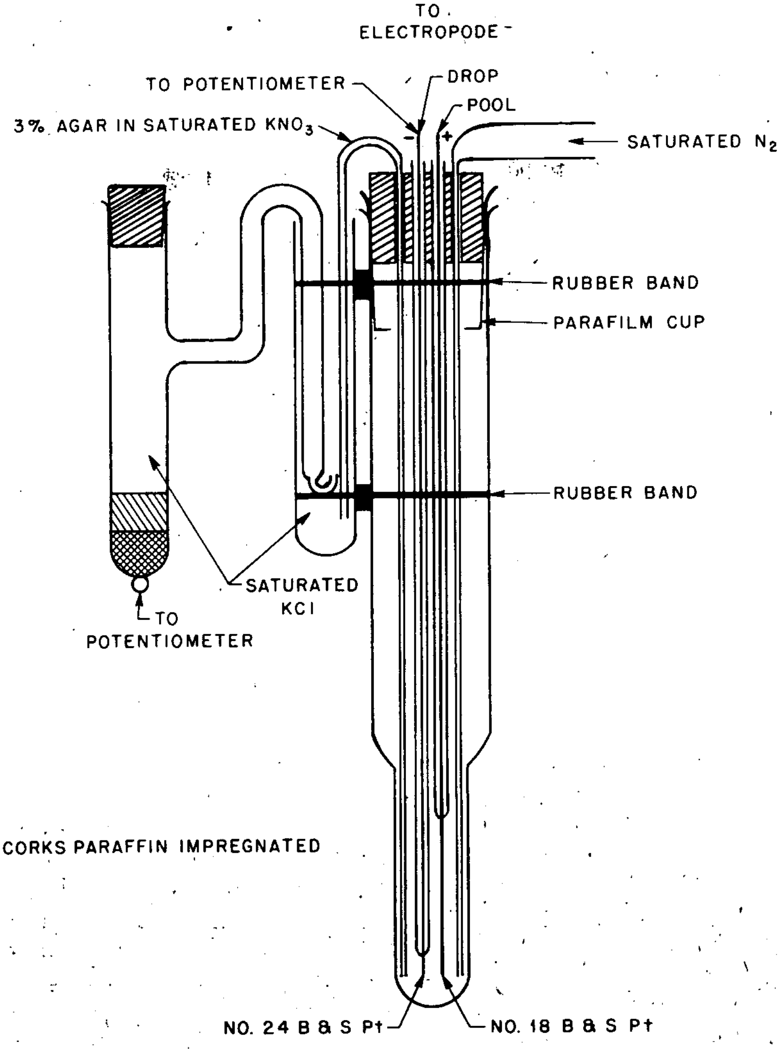


Fig. 4.22 — Microcell for polarographic studies.

A typical curve is shown in Fig. 4.25 in which the deposition of polonium is indicated at 0.488 and 0.504 volt. The inflection points at 0.23 and 0.25 volt are ascribed to platinum. It is well known that in hydrochloric acid solutions platinum is dissolved at the anode because of free chlorine liberated by alpha bombardment. Haring showed that

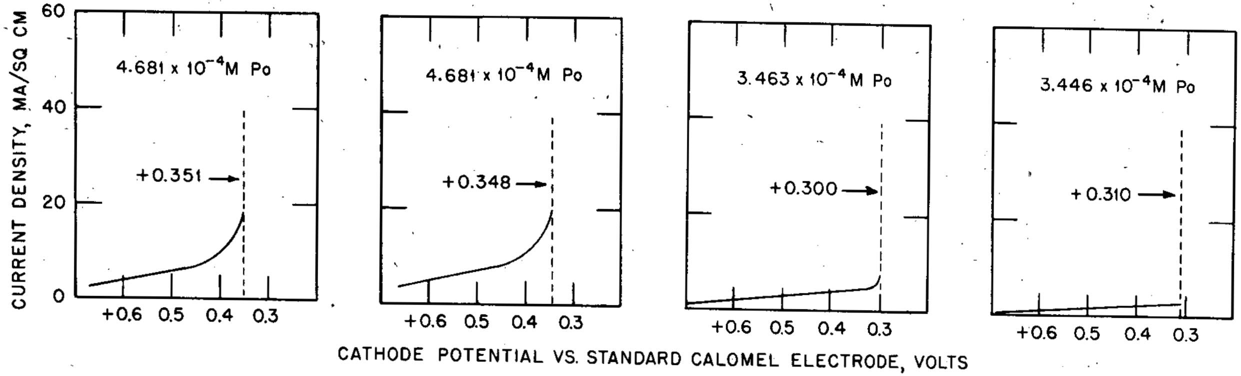


Fig. 4.23—Decomposition potential of 4.44 × 10^{-4}M polonium, at 25°C, in 1.5N HNO_3.

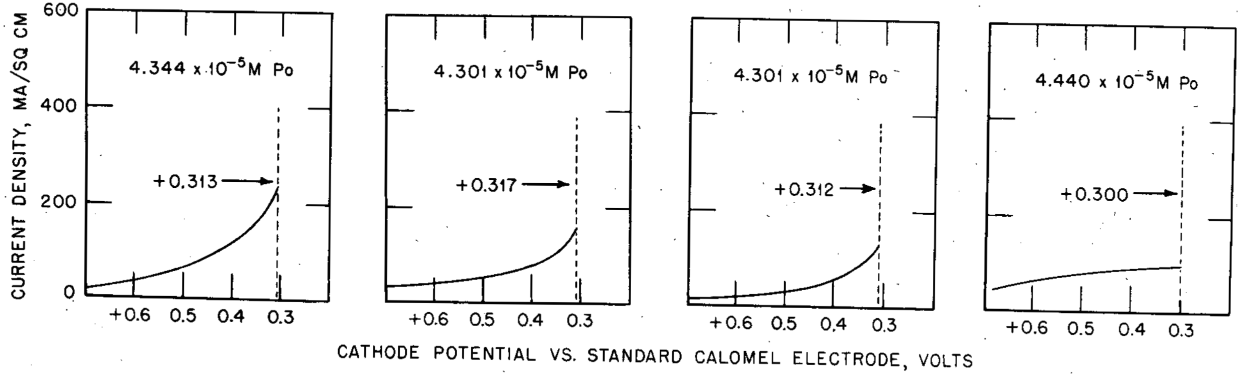


Fig. 4.24—Decomposition potential of 4.44 × 10^{-5}M polonium, at 25°C, in 1.5N HNO_3.

Table 4.11—Decomposition Potential (E_d) for Polonium (10^{-3}N) Vs. the Standard Calomel Electrode

Assume n = 2				Assume n = 4			
E_d at concentration given, volts	Voltage correction, volts	E_d at 10^{-3}N, volts	Volts deviation, volts	E_d at concentration given, volts	Voltage correction, volts	E_d at 10^{-3}N, volts	Volts deviation, volts
			4.44×10^{-4}M Polonium				
+0.350	+0.0015	+0.3515	+0.0183	+0.351	−0.0037	+0.3473	+0.0273
+0.347	+0.0015	+0.3485	+0.0153	+0.348	−0.0037	+0.3443	+0.0243
+0.303	+0.0015	+0.3045	−0.0287	+0.302	−0.0037	+0.2983	−0.0217
+0.313	+0.0015	+0.3145	−0.0187	+0.312	−0.0037	+0.3083	−0.0117
+0.323	+0.0015	+0.3245	−0.0087	+0.323	−0.0037	+0.3193	−0.0007
+0.336	+0.0015	+0.3375	+0.0043	+0.336	−0.0037	+0.3323	+0.0123
+0.345	+0.0015	+0.3465	+0.0133	+0.345	−0.0037	+0.3413	+0.0213
+0.330	+0.0015	+0.3315	−0.0017	+0.330	−0.0037	+0.3263	+0.0063
			4.44×10^{-5}M Polonium				
+0.313	+0.0311	+0.3441	+0.0109	+0.313	+0.0111	+0.3241	+0.0041
+0.317	+0.0311	+0.3481	+0.0149	+0.317	+0.0111	+0.3281	+0.0081
+0.312	+0.0311	+0.3431	+0.0099	+0.312	+0.0111	+0.3231	+0.0031
+0.303	+0.0311	+0.3341	+0.0009	+0.303	+0.0111	+0.3141	−0.0059
+0.298	+0.0311	+0.3291	−0.0041	+0.298	+0.0111	+0.3091	−0.0109
+0.300	+0.0311	+0.3311	−0.0021	+0.300	+0.0111	+0.3111	−0.0089
+0.285	+0.0311	+0.3161	+0.0171	+0.285	+0.0111	+0.2961	−0.0239
+0.285	+0.0311	+0.3161	+0.0171	+0.285	+0.0111	+0.2961	−0.0239
	Av.	+0.3332 ± 0.0116			Av.	+0.3200 ± 0.0134	

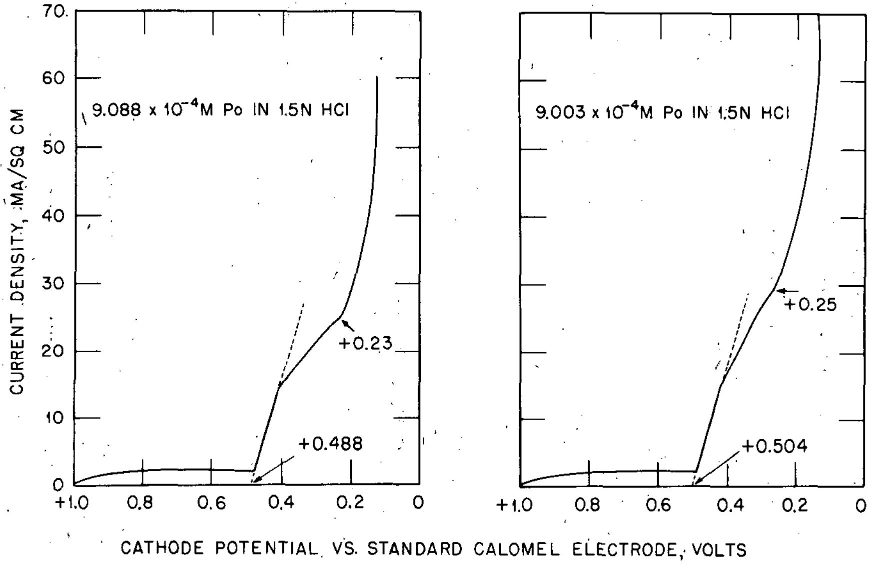


Fig. 4.25—Decomposition potential of 10^{-3}M polonium in 1.5N HCl.

10^{-2}M platinum solutions in 1.5N hydrochloric acid without polonium showed an inflection point in the polarogram at +0.164 volt (Fig. 4.26). The data from 15 runs in 1.5N hydrochloric acid are shown in Table 4.12. Slightly more constant values for the calculated decomposition potentials in 10^{-3}M polonium solutions are obtained on the assumption that the oxidation change in hydrochloric acid is 4 rather than 2.

Power[56,57] studied the deposition of polonium from solutions of 4.7N hydrochloric acid. He used a silver-silver chloride reference electrode and used cathodes of either gold or platinum foil. The apparatus permitted an alternation in the direction of the changing applied potential.

Potential was changed at the rate of approximately 1 volt/hr. The curve in Fig. 4.27 illustrates the operation of the apparatus. As the cathode potential is made more negative from A to B, there is a small constant ionization current due to alpha particles from the solution passing through the platinum- or gold-foil cathode and entering the ionization chamber. When a potential of +0.38 volt is reached, polonium begins to deposit on the cathode and consequently a sharp rise in the ionization current takes place. The direction of the change in potential is reversed at C, although polonium continues to deposit on the cathode until at D where a potential of +0.49 volt is reached. As the cathode

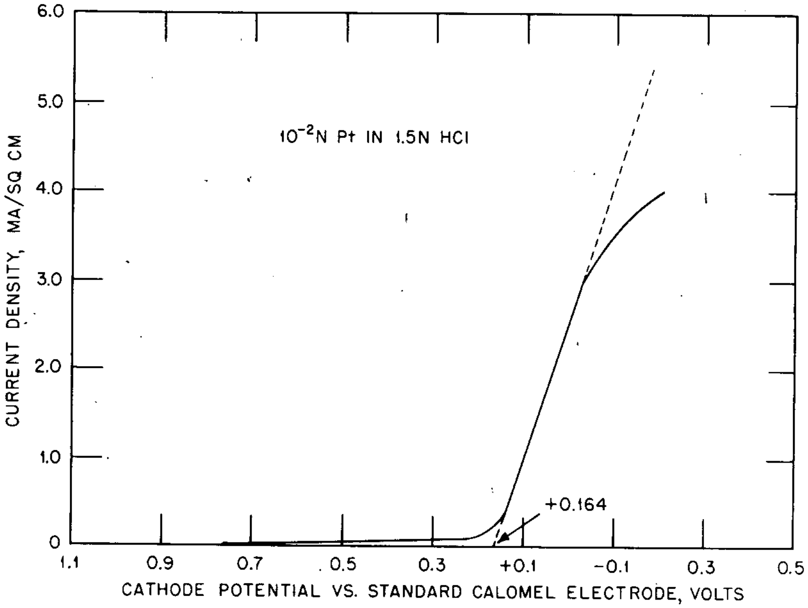


Fig. 4.26—Polarogram inflection point which is attributable to platinum.

Table 4.12—Valence of Polonium in 1.5N HCl

Concentration by analysis, M	Concentration corrected, M	E observed vs. standard calomel electrode	E corrected to 10^{-3}M		Deviations, mv	
			n = 2	n = 4	n = 2	n = 4
8.651×10^{-4}	9.137×10^{-4}	+0.473	+0.465	+0.465	−36	−29
8.651×10^{-4}	9.088×10^{-4}	+0.497	+0.489	+0.489	−12	−5
8.651×10^{-4}	9.088×10^{-4}	+0.488	+0.480	+0.480	−21	−14
8.651×10^{-4}	9.003×10^{-4}	+0.504	+0.496	+0.496	−5	+2
8.651×10^{-4}	9.003×10^{-4}	+0.514	+0.506	+0.506	+5	+12
8.317×10^{-5}	8.360×10^{-5}	+0.497	+0.520	+0.504	+19	+10
8.317×10^{-5}	8.317×10^{-5}	+0.496	+0.519	+0.503	+18	+9
8.317×10^{-5}	8.317×10^{-5}	+0.494	+0.517	+0.501	+16	+7
8.317×10^{-5}	8.275×10^{-5}	+0.497	+0.520	+0.504	+19	+10
8.317×10^{-5}	8.233×10^{-5}	+0.501	+0.524	+0.508	+23	+14
4.822×10^{-4}	4.896×10^{-4}	+0.479	+0.479	+0.475	−22	−19
4.822×10^{-4}	4.871×10^{-4}	+0.489	+0.489	+0.485	−12	−9
4.822×10^{-4}	4.846×10^{-4}	+0.525	+0.525	+0.521	+24	+27
4.822×10^{-4}	4.846×10^{-4}	+0.491	+0.491	+0.487	−10	−7
4.822×10^{-4}	4.846×10^{-4}	+0.492	+0.492	+0.488	−9	−6
		Average	+0.501	+0.494	+16.7	+12.0

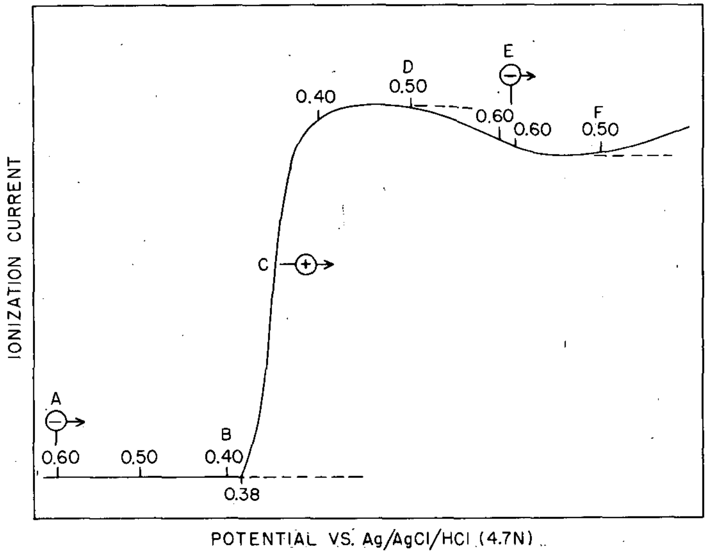


Fig. 4.27 — Typical ionization current recorded during polarographic run. ⊖→, potential changing toward negative values from left to right. ⊕→, potential changing toward positive values from left to right.

becomes more positive, the polonium begins to dissolve, thus reducing the ionization current. At E the cathode starts to become more negative again until at F a cathode potential of +0.49 volt is reached and polonium again plates out on the cathode. Power found that the potential at which the first deposition of polonium began was not reproducible and that the ionization current never returned to the value observed before the initial polonium deposit. Evidently a residual amount of polonium remained on the cathode. The inflection points at D and F, indicating the decomposition potential of the solution, were reproducible as the cathode potential was varied any number of times above and below this value. A continuous record of the ionization current is shown in Fig. 4.28. The inflection point at +0.49 volt (vs. Ag-AgCl) was reproduced with the best precision. After several reversals of direction, an inflection point appeared at +0.56 volt. Since this inflection did not appear when this potential was passed several times in the early part of the experiment, it was assumed to be due to the presence of dissolved platinum in the solution. The inflection point at 0.27 volt may be due to the deposition of polonium from a different oxidation state.

11.4 *Oxidation States of Polonium in Acid Solutions.* The oxidation states of +2 and +4 have been established by Joy[5] for the chlorides in

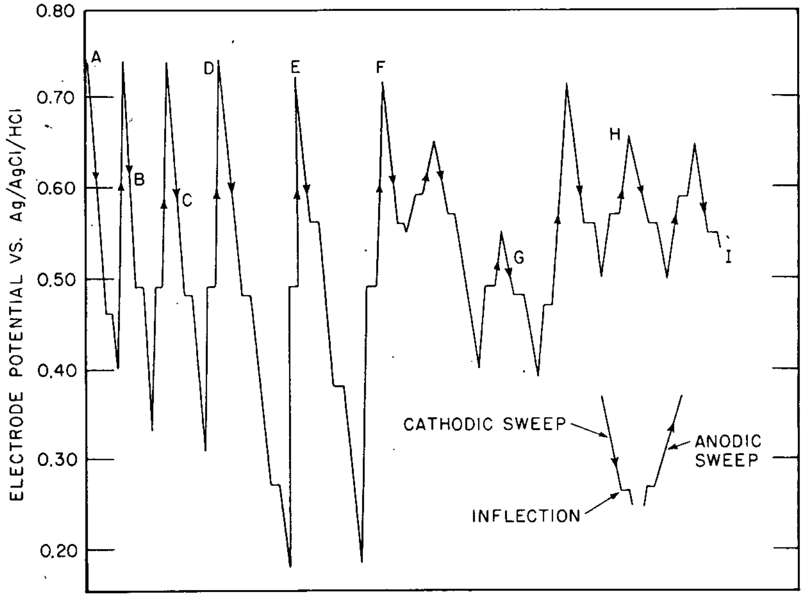


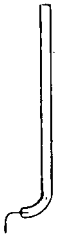
Fig. 4.28—Typical decomposition-potential record.

the crystalline state. Experiments to determine the oxidation states in acid solutions have not been conclusive. Shoemaker[59] made a polarographic study at Mound Laboratory of the reduction of polonium in solutions of hydrochloric acid and in nitric acid by use of a rotating platinum electrode. His results suggested two equal reduction steps in hydrochloric acid. In nitric acid the reduction to the metal appears to take place in a single step. The cell which Shoemaker used is shown in Fig. 4.29. The cathode potentials were measured against a saturated calomel electrode. A typical curve is shown in Fig. 4.30.

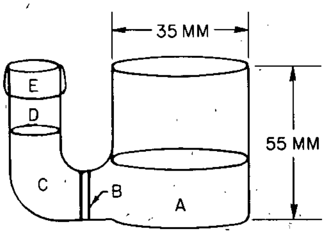
The polarogram was obtained in a 6N hydrochloric acid solution which was 0.806×10^{-5}M in polonium. The initial rise in the curve was shown by Shoemaker (in blank runs) to be due to the reduction of free chlorine to the chloride ion. The second inflection point at −0.1 volt was always present in hydrochloric acid solution, but the height of the wave was difficult to determine. Shoemaker interpreted the approximate equality of the wave heights to mean a probable equal reduction change of +4 to +2 and from +2 to 0, respectively.

A typical curve for the reduction of polonium in 1.5M nitric acid is shown in Fig. 4.31. The concentration of polonium was 0.42×10^{-4}M. Similar curves were obtained in 3M nitric acid solutions.

A different method of determining the oxidation states of polonium in solution was used by Payne and Nelson.[60] They obtained evidence to indicate that the two oxidation states of polonium in hydrochloric acid solution are + 3 and + 4. They measured the potential difference between a platinum or gold electrode and a silver–silver chloride reference electrode during the auto-oxidation of polonium from the metallic state to the higher oxidation states in hydrochloric acid solution. They found that a platinum electrode placed in a solution containing suspended particles of tellurium established a potential identical with that given when the tellurium metal is packed around the electrode. A lower limit of 10^{-4}M tellurium can be used for potential measurements. A similar procedure was used with suspensions of polonium. If the polonium is reduced to the metal by the addition of stannous chloride (in slight excess), the finely divided metallic polonium causes the platinum or gold



ELECTRODE



CELL

Fig. 4.29—Shoemaker's polarographic cell. A, sample (10 ml); B, coarse glass filter plate; C, agar salt bridge of saturated KNO_3; D, saturated KNO_3 solution; E, paraffin coating.

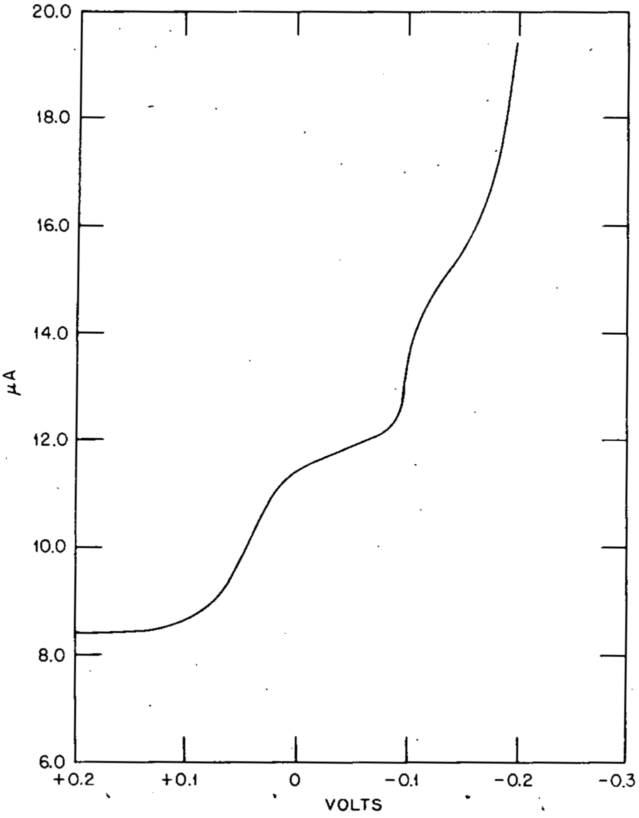


Fig. 4.30 — Specimen curve showing valence change as a function of electrode potential.

electrode to attain a characteristic potential. The alpha bombardment of the solution produces oxidants which first oxidize the excess stannous tin to the stannic form, and, when the tin reaction is completed, the polonium metal is oxidized at a constant rate. The potential of the electrode indicated these changes and showed that the polonium oxidation takes place in two steps. The potential of the indicator electrode with respect to the silver–silver chloride electrode during the autooxidation of polonium is shown in Fig. 4.32. The color changes in the solution, as indicated in the figure, are consistent with the red color observed by Joy[5] for $PoCl_2$ and the yellow color for $PoCl_4$; however, Payne and Nelson concluded that the second oxidation step is from + 3

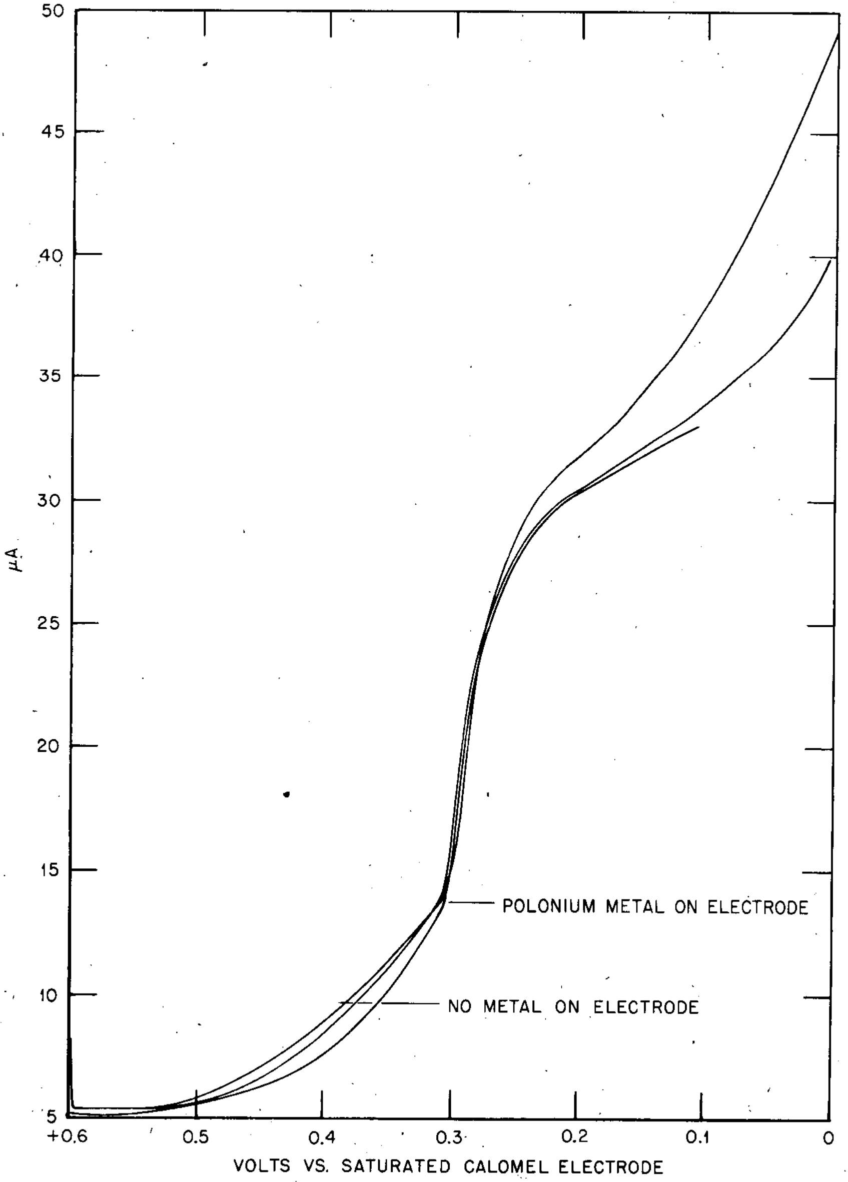


Fig. 4.31—Valence change from duplicate experiments. 0.42×10^{-4}M polonium in 1.5M HCl.

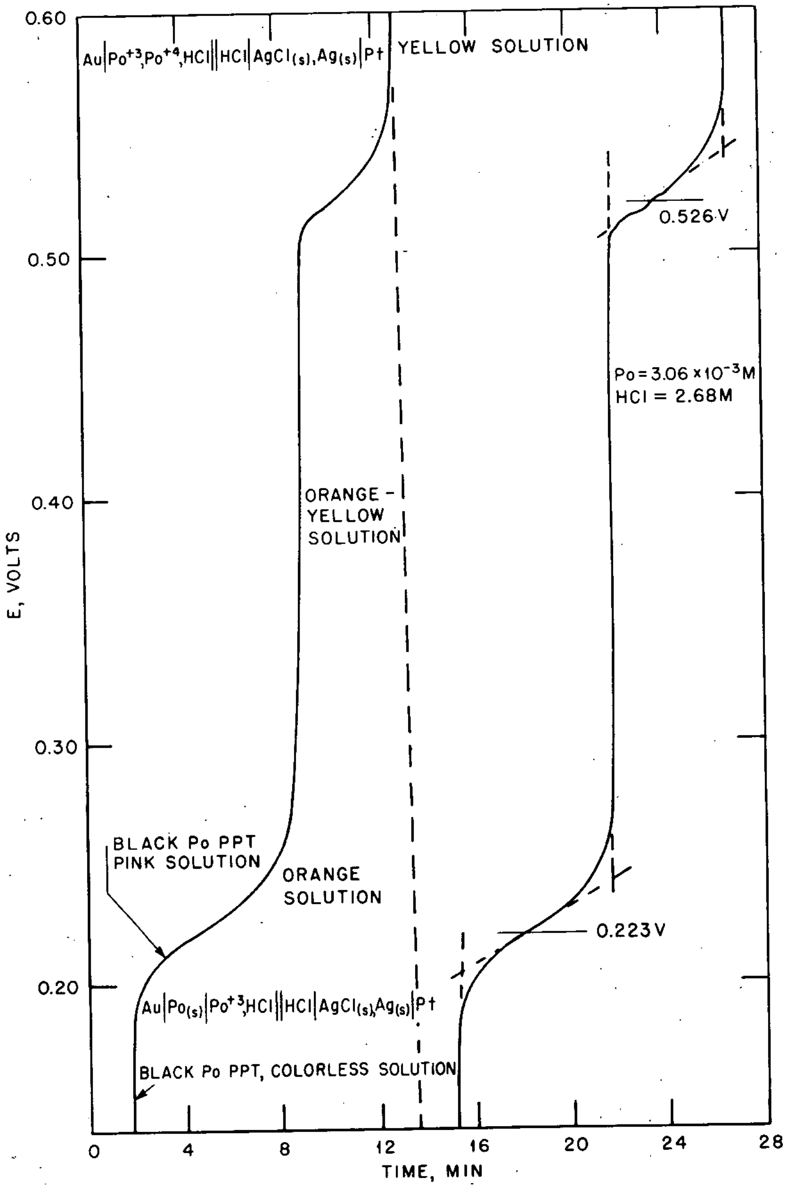


Fig. 4.32—Potential of the cells measured, at 25°C, by the precipitation-oxidation method. (Two complete cycles of same solution shown.)

to + 4. They based their conclusion upon a study of the time required to complete the second oxidation reaction of polonium. They found that in a given solution the time required to complete the reaction is independent of the polonium concentration. In a 3.06×10^{-3}M polonium solution in 2.68M hydrochloric acid, an average time of 4.2 min was required to complete the second oxidation step. When a mixture of polonium isotopes (of mass 208 and 209) was used in the same concentration of hydrochloric acid, the second oxidation reaction required 42 min, as indicated in Fig. 4.33. The time to complete the reaction was 10 times that required for Po^{210}, and, since the specific activity of the Po^{208} Po^{209} mixture was about one-ninth that of Po^{210}, the auto-oxidation time was fairly close to the expected value. When ferrous iron, which has an oxidation potential quite close to the upper potential for polonium, was added in equal molecular concentration with the polonium, the time to complete the second oxidation step was doubled. Figure 4.34 shows the curves obtained with a mixture of ferrous iron and polonium. Curves A and B in Fig. 4.35 show that the time required to complete the oxidation of the iron and polonium is directly proportional to the moles of iron and polonium present and that polonium and iron are equivalent mole for mole. Cuprous copper is oxidized to the cupric state at a potential close to that of the second step in the polonium oxidation. Experiments similar to those conducted with ferrous iron showed that the second oxidation step for polonium in hydrochloric acid is also equivalent to the oxidation of cuprous copper to the cupric state.

The number of electrons involved in the second step in the auto-oxidation of polonium can be determined by use of the following equation:

$$T = \frac{nM_{Po} + Eq_{Fe}}{kM_{Po}} \quad (\text{or } Eq_{Cu}) \tag{4.14}$$

where T = the time of oxidation in minutes
n = the equivalents of polonium per mole
Eq_{Fe} = the number of equivalents of ferrous iron
k = the number of equivalents of oxidant produced per mole of polonium per minute

Equation 4.14 may be rearranged to

$$\frac{Eq_{Fe}}{M_{Po}} = kT - n \tag{4.15}$$

When Eq_{Fe}/M_{Po} is plotted against T, straight lines, as shown in Fig. 4.36, are obtained. When k = 0 the lines intercept the Y axis close to

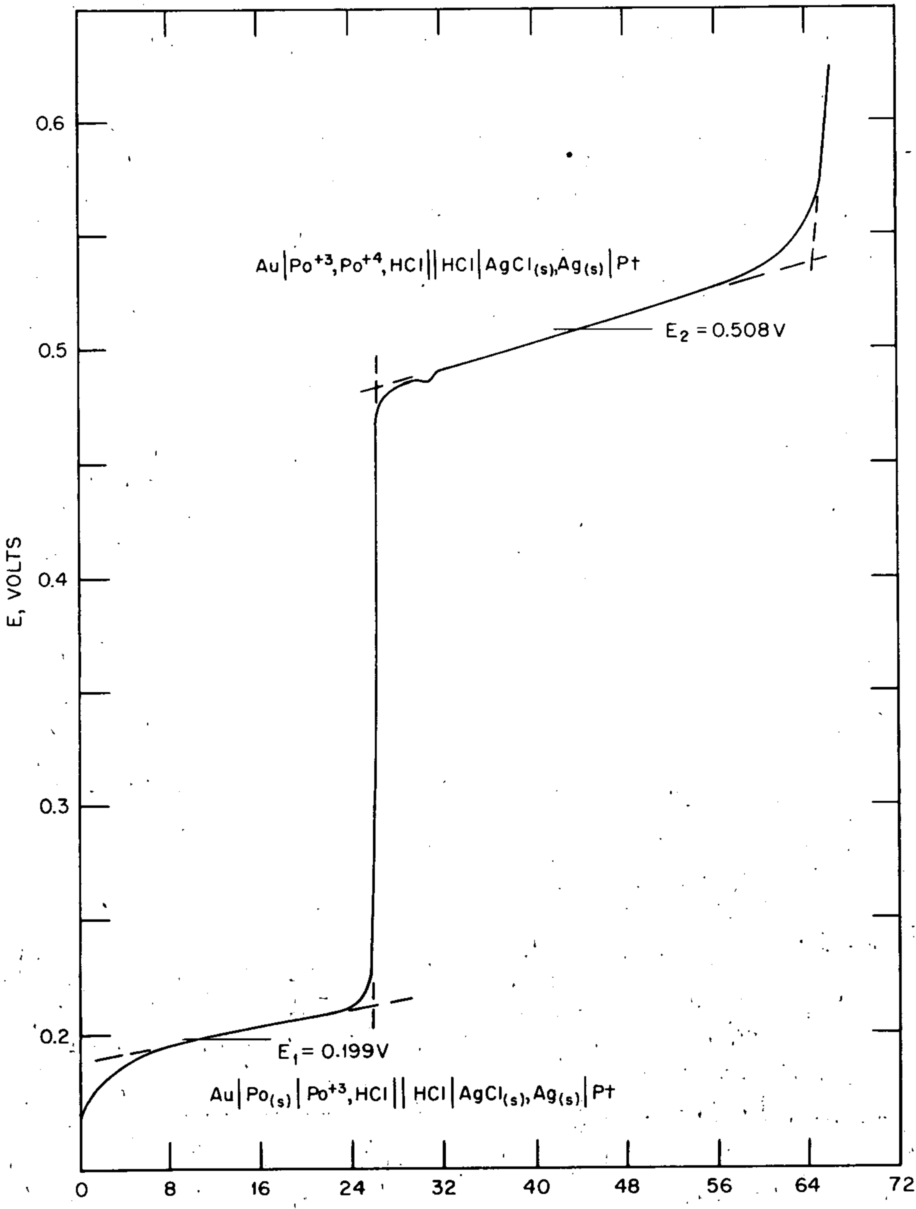


Fig. 4.33—Potential of the cells, at 25°C, as measured by precipitation method. Concentrations: Po = 2.218×10^{-3}M; HCl = 2.679M.

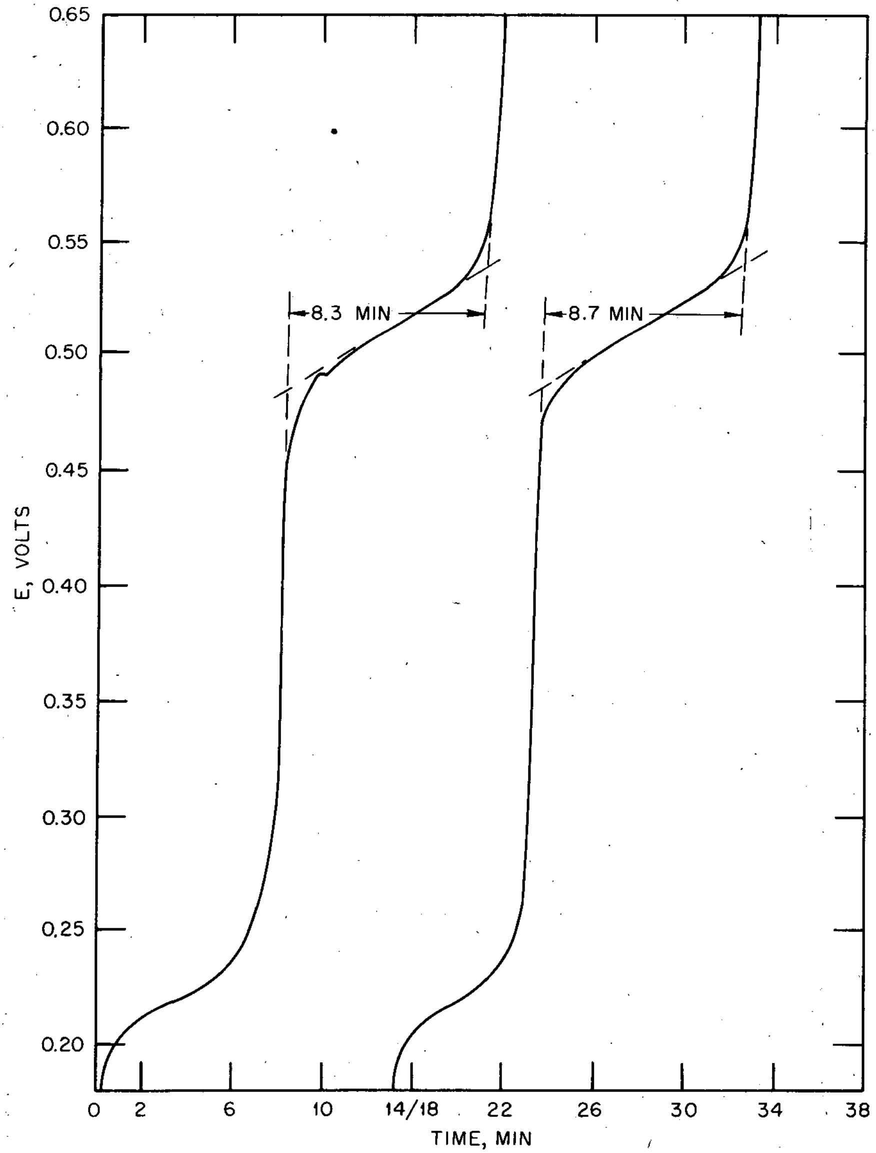


Fig. 4.34—Auto-oxidation of polonium from lower to +4 state, using iron as standard. (Two cycles shown.) Concentrations: Po = 5.66 × 10^{-6}M; Fe = 5.50 × 10^{-6}M.

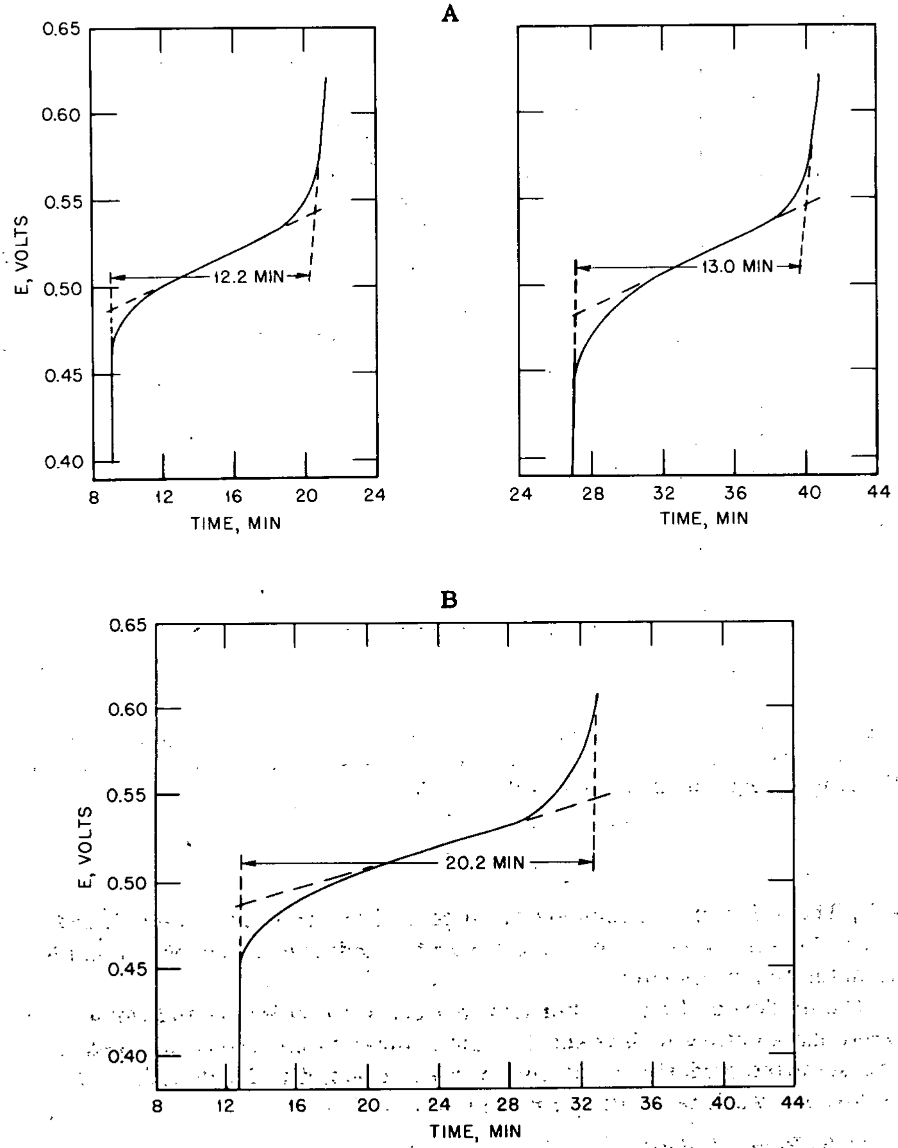


Fig. 4.35—Auto-oxidation of polonium from lower to +4 state using iron as a standard. Concentrations: A, Po = 5.66×10^{-6}M; Fe = 11.0×10^{-6}M. B, Po = 5.37×10^{-6}M; Fe = 22.0×10^{-6}M.

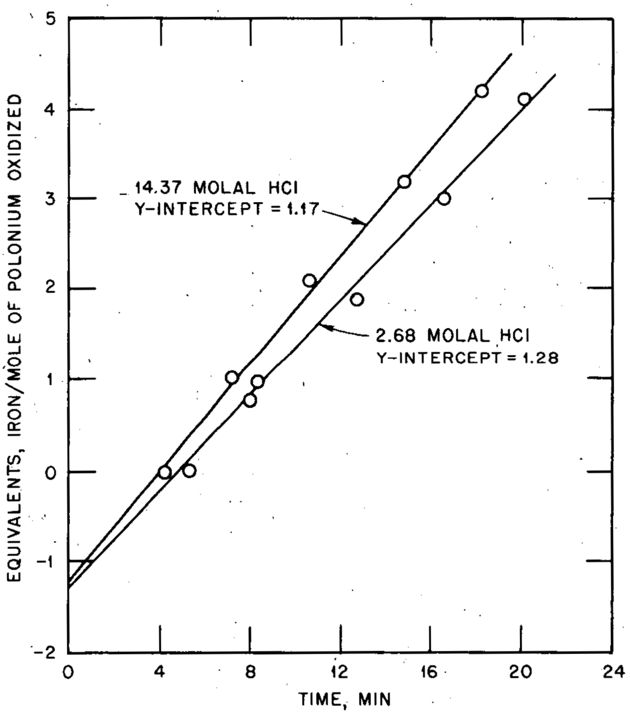


Fig. 4.36—Number of electrons lost by the reduced polonium ion in the oxidation to the +4 state. Iron used as standard. Least-squares determination of n in the equation equivalents Fe/moles Po = $k_{Fe}T - n$.

−1. The value of n is thus shown to be 1. Similar results were found when the experiments were made with the addition of cuprous chloride to solutions of polonium.

The evidence of Shoemaker and that obtained by Payne and Nelson are contradictory with respect to the number of electrons involved in the stepwise oxidation of polonium in solutions of hydrochloric acid. Additional work is needed to resolve the problem.

11.5 *Redox Potential of Polonium in Solutions of Hydrochloric Acid.* Payne and Nelson calculated the standard potentials of the Po-Po^{+3} and the Po^{+3}-Po^{+4} reactions on the assumption that the Nernst equation is followed. Their results are shown in Fig. 4.37. In curve A the reaction Po → Po^{+3} is assumed, whereas in curve B the reaction Po → Po^{+2} is assumed. Payne and Nelson point out that better agreement for the

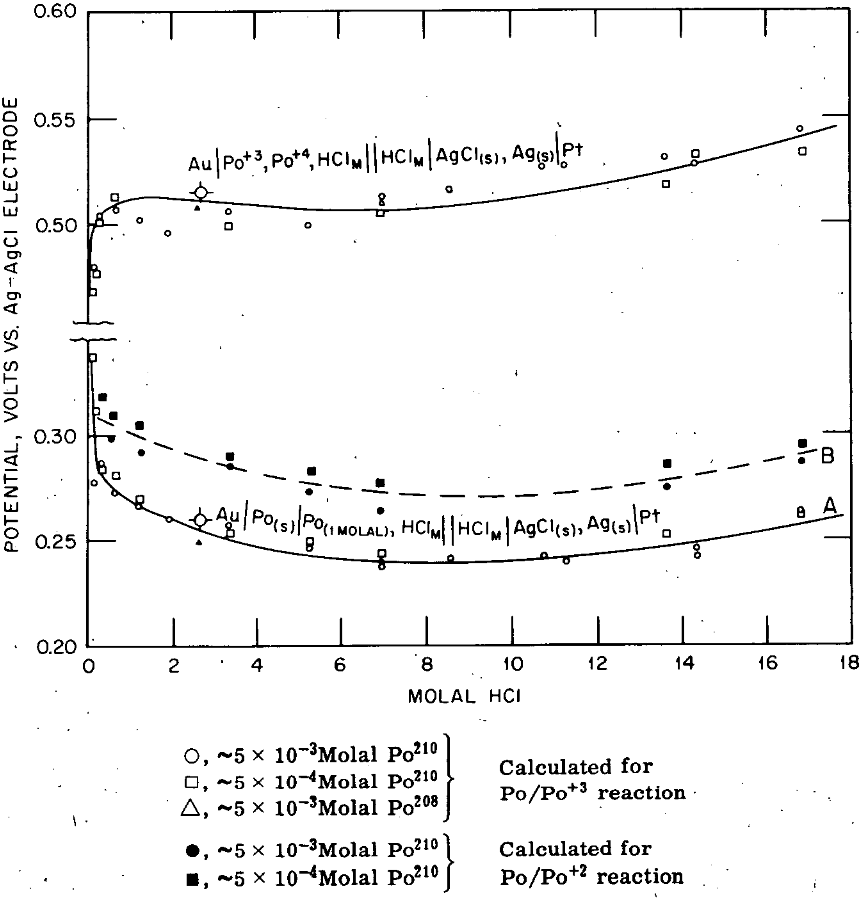


Fig. 4.37—Calculated values for the normal potential of the Po-Po^{+3} (or Po^{+2}) couple in varying concentrations of HCl.

standard potential is obtained from observations taken at different concentrations when Po → Po^{+3} is assumed. Table 4.13 shows the redox potentials in various acid solutions which have been proposed by various workers.

12. POLONIUM COMPOUNDS WITH METALS

12.1 *Zinc Polonide.* A crystalline compound of zinc and polonium was prepared by Fauble,[61] who heated 6.04 curies of purified polonium

Table 4.13—Standard Cathode Potential of Polonium

Method	Po/Po^{+2}, volts	Po/Po^{+3}, volts	Po/Po^{+4}, volts	Author
In Nitric Acid (~1 × 10^{-8}M Po)				
Deposition on metals	~0.8			Johnson
Critical deposition potential	0.84	0.76	0.72	Paneth, Hevesy
Critical deposition potential†		0.53	0.78	Haissinsky
Critical deposition potential	0.87	0.79	0.75	Schneidt
Critical deposition potential	0.89	0.81	0.77	Joliot
Estimated from chemical behavior			~0.4 ± 0.1	Reichinstein
			~0.75	Benjamin
In Nitric Acid (~1 × 10^{-5}M Po)				
Critical deposition potential	0.632	0.586	0.563	Moshier
Polarography	0.668	0.639	0.624	Haring
Plating to equilibrium	0.70	0.63	0.59	Bowman, Krikorian
In Hydrochloric Acid (9 × 10^{-5} to 9 × 10^{-4}M Po)				
Polarography			0.784	Haring
(~3.6 × 10^{-4} to 1.3 × 10^{-2}M Po)				
Oxidation-precipitation‡		0.498	0.556 (calc.)	Nelson, Payne
In H_2SO_4 (0.5N), Po = 6 × 10^{-9}M				
Critical deposition potential	0.87	0.79	0.75	Joliot
In H_2SO_4 (>4N), Po = 6 × 10^{-9}M				
Critical deposition potential	0.61	0.53	0.49	Haissinsky, Guillot
In CH_3COOH (0.3N), Po = 3 × 10^{-9}M				
Critical deposition potential	0.88	0.80	0.76	Joliot
In CH_3COOH (1.12N), Po = 3 × 10^{-9}M				
Critical deposition potential	0.72	0.64	0.60	Joliot
In Oxalic Acid (1N), Po = 3.8 × 10^{-9}M				
Critical deposition potential	0.54	0.46	(0.41)	Joliot
In Sodium Hydroxide (1.5N)				
Polarography	−0.315	−0.360	−0.382	Haring
Plating to equilibrium			0.37 to −0.42	Bowman, Krikorian

† Po^{+3}/Po^{+4} = ~1.5 volts.
‡ Po^{+3}/Po^{+4} = 0.739 volt.

in vacuo with 2.165 mg of zinc. As the polonium was moved closer to the zinc by heating to 350°C, crystals of zinc polonide appeared in the quartz tube. Crystals of zinc polonide are shown in Fig. 4.38.

Brocklehurst and Vassamillet[62] obtained X-ray data on zinc polonide. They found it to have a face-centered cubic structure of the zinc-blende type with $a_0 = 6.28 \pm 0.02$ A. A comparison of zinc polonide with ZnS, ZnSe, and ZnTe tends to confirm the formula ZnPo for zinc polonide. The calculated density of ZnPo is 7.39 g/cu cm.

12.2 *Lead Polonide.* Brocklehurst and Vassamillet[63–66] observed a new structure in a sample of pure polonium after $13\frac{1}{2}$ per cent of it had decayed. It was a face-centered cubic structure of NaCl type with $a_0 = 6.60 \pm 0.003$ A. It was believed to be PbPo. Its calculated density is 9.64 g/cu cm.

12.3 *Platinum Polonide.* A compound of platinum and polonium was prepared by A. W. Martin in 1949, and its crystal structure was studied by Goode and Timma.[67] They assigned it a hexagonal structure, probably of the $Cd(OH)_2$ type. Two preparations of the compound were made with lattice parameters in close agreement. The first preparation with $\frac{1}{2}$ per cent of the polonium decayed gave $a_0 = 4.104 \pm 0.004$ A and C = 1.366; the second preparation with the same percentage decay gave $a_0 = 4.102 \pm 0.002$ A and C = 1.371. The formula, $PtPo_2$, was chosen after comparison of the parameters with those of PtS_2, $PtSe_2$, and $PtTe_2$. The calculated density of $PtPo_2$ is 12.47 g/cu cm.

12.4 *Nickel Polonide.* A compound of nickel and polonium was prepared at Mound Laboratory by A. W. Martin and L. K. Lantz in 1949 for study by the Mound Laboratory X-ray group. X-ray studies were made by Goode,[68–71] who determined a hexagonal structure with $a_0 = 3.976 \pm 0.008$ A and C = 1.425 at $\frac{1}{2}$ per cent of polonium decayed. The formula NiPo was chosen as the most probable. Its calculated density is 11.53 g/cu cm. Witteman and Spillert[72] report experiments indicating alloy formation with composition varying continuously between NiPo and $NiPo_2$.

12.5 *Silver Polonide.* Goode[68–71] prepared a compound of polonium and silver by distilling about 1 curie of purified polonium upon silver wire in an evacuated quartz capillary tube. Compound formation was accomplished by heating to approximately 400°C at a pressure of 10^{-5} mm Hg. The compound was observed to decompose at approximately 559°C. X-ray powder patterns showed 62 lines ascribed to silver polonide. Attempts to index the lines in the orthorhombic system were not entirely satisfactory, but it was concluded that the structure of the compound was either orthorhombic or monoclinic, or both. In the absence of conclusive data on the structure of Ag_2S, Ag_2Se, and Ag_2Te, no

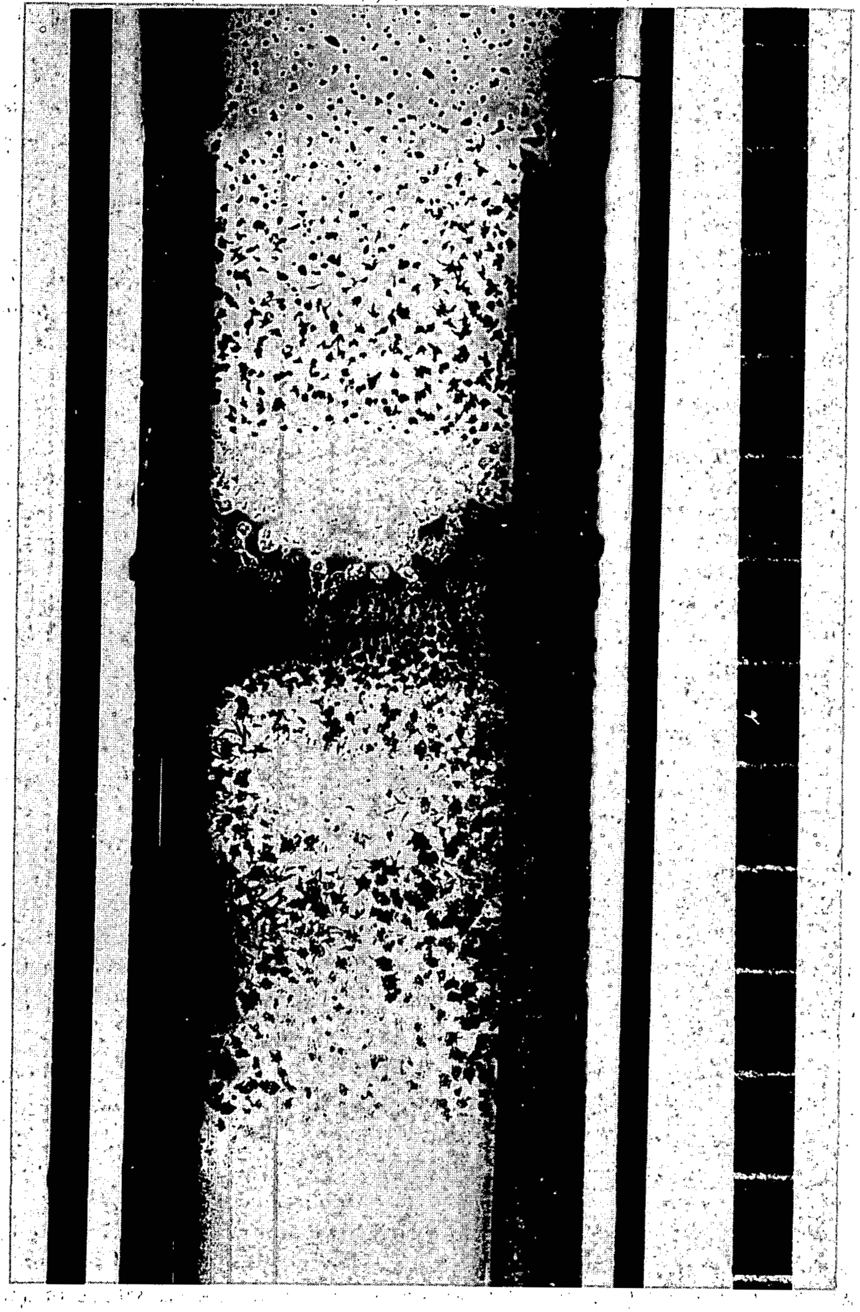


Fig. 4.38—Crystals of zinc polonide.

conclusion was reached regarding the most probable formula for the silver polonide.

12.6 *Beryllium Polonide.* A compound of beryllium and polonium was prepared at the Los Alamos Scientific Laboratory[73] by heating beryllium powder in a capillary tube *in vacuo* at 600°C and heating polonium at the other end of the capillary to 575°C. X-ray diffraction patterns showed a face-centered cubic structure similar to BeS, BeSe, and BeTe. The lattice constant is 5.827 A, and the calculated density is 7.35 g/cu cm.

12.7 *Calcium Polonide.* A compound of calcium and polonium was prepared at the Los Alamos Scientific Laboratory,[74] and its crystal structure was determined by X-ray diffraction. Nineteen diffraction lines were observed, all of which indexed a face-centered cubic crystal of the NaCl type with a lattice constant of 6.51 ± 0.004 A at approximately 25°C.

12.8 *Sodium Polonide.*[63–66] A face-centered cubic crystalline compound was observed in a Pyrex capillary in which a sample of polonium had been stored until 32 per cent of it had decayed. The lattice constants of the crystalline substance agreed quite well with the probable values for Na_2Po, as predicted by comparison with Na_2O, Na_2S, Na_2Se, and Na_2Te. The average of four patterns having the largest number of lines gave $a_0 = 7.473 \pm 0.004$ A. The calculated density is 4.08 g/cu cm.

REFERENCES

1. D. Mendeléev, J. Chem. Soc., 55: 649 (1889).
2. F. Paneth and A. Johanssen, Ber., 55: 2647 (1922).
3. A. W. Martin, Determination of the Formula of an Oxide of Polonium, Report MLM-855, July 7, 1953.
4. G. Moulton and J. Farr, The Preparation and Reduction of Polonium Dioxide, Report LA-1523A, March 1953.
5. E. F. Joy, The Chlorides of Polonium, Their Preparation and Properties, Presented at the 125th Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, Kansas City, Mar. 31, 1954.
6. T. J. LaChapelle, Jr., J. J. Howland, Jr., B. B. Brody, L. Niedrach, B. M. Abraham, and A. Martin, Preliminary Work on Oxidation States of Polonium and Preparation of Some of Its Compounds, Final Report No. 31, Report MLM-M-529, May 1, 1946.
7. L. Dede and W. Russ, Ber., 61B: 2451-2459 (1928).
8. D. Glick, J. Chem. Educ., 16: 68-76 (1939).
9. D. H. Reynolds, Letter to E. F. Joy, Report MLM-46-12-116, Dec. 31, 1946.
10. E. F. Joy, Progress Report, Report MLM-175, Aug. 1–31, 1948.
11. E. F. Joy, Progress Report, Report MLM-252, Dec. 1–31, 1948.

12. L. E. Marchi, M. M. Haring, and M. B. Hicks, The Polonium-Iodine Ratio, Final Report No. 35, Report MLM-M-636, Aug. 22, 1946.
13. D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry of the Fifth- and Sixth-group Nonmetallic Elements," p. 295, Prentice-Hall, Inc., New York, 1944.
14. F. Leitz, Jr., and L. Coulter, A Study of the Polonium-Fluorine System, Final Report No. 44, Report MLM-M-198, July 24, 1947.
15. R. Wehrmann, The Electrodeposition of Polonium from Hydrofluoric Acid Solutions, Ad Interim Report No. 10, Report MLM-18, Nov. 30, 1947.
16. P. Curie and M. Curie, Compt. rend., 127: 176 (1898).
17. J. M. Goode, Quarterly Progress Report, Report MLM-535, p. 15, Feb. 26, 1951.
18. E. Orban, Progress Report, Report MLM-M-159, June 1–15, 1947.
19. C. E. Shoemaker, unpublished results, 1953.
20. M. Haissinsky, Trans. Electrochem. Soc., 70: 351 (1936).
21. A. Fainberg, S. Barth, and R. Staniforth, private communication, Mar. 11, 1946.
22. J. W. Schulte, Research on the Electrodeposition of Polonium, Final Report No. 14, Report MLM-M-573, May 1, 1946.
23. B. B. Harlow, Laboratory Notes, Report MLM-M-76, Mar. 21, 1947.
24. M. M. Haring, The Solubility of Polonium Oxide in Sodium Hydroxide, Report MLM-45-9-43, Sept. 12, 1945.
25. A. G. Samartseva, Trav. inst. état radium U.S.S.R., 4: 253-303 (1938).
26. A. Fainberg, S. Barth, and M. M. Haring, Some Colloid Properties of Polonium, Report MLM-M-467, Mar. 11, 1946.
27. S. Barth, A. Fainberg, M. M. Haring, and R. A. Staniforth, Some Colloid Properties of Polonium, Report MLM-M-197, July 24, 1947.
28. W. M. Clark, "Determination of Hydrogen Ions," 3d ed., The Williams & Wilkins Co., Baltimore 2, Md., 1928.
29. S. Barth and W. H. Power, Progress Report, Report MLM-196, Sept. 1–30, 1948.
30. S. Barth and W. H. Power, Progress Report, Report MLM-216, Oct. 1–31, 1948.
31. S. Barth and W. H. Power, Progress Report, Report MLM-238, Nov. 1–30, 1948.
32. S. Barth and W. H. Power, Progress Report, Report MLM-253, Dec. 1–31, 1948.
33. F. Paneth, Kolloid-Z., 13: 1-4 (1913).
34. G. Hevesy, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa, 127: 1787-1798 (1918).
35. H. Raudnitz, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa, 136: 447-451 (1928).
36. I. E. Starik, Z. physik. Chem., A157: 269-284 (1931).
37. R. A. Staniforth and S. Barth, Progress Report, Report MLM-M-56, Feb. 15–28, 1947.
38. R. A. Staniforth and S. Barth, Progress Report, Report MLM-M-70, Mar. 1–15, 1947.
39. R. A. Staniforth and S. Barth, Progress Report, Report MLM-M-85, Mar. 15–31, 1947.

40. R. A. Staniforth and S. Barth, Progress Report, Report MLM-M-100, Apr. 1–15, 1947.
41. R. A. Staniforth and S. Barth, Progress Report, Report MLM-M-115, Apr. 15–30, 1947.
42. R. A. Staniforth and S. Barth, Progress Report, Report MLM-M-175, June 16–30, 1947.
43. W. C. McCluggage, Quarterly Progress Report, Report MLM-405-2, October, November, and December 1949, p. 71.
44. Progress Report, Report WASH-82, December 1952, p. 11.
45. Progress Report, Report WASH-86, April 1953, p. 6.
46. D. J. Hunt, Polonium Complexes in Chloride Solutions by Absorbancy Studies, Report MLM-979, June 7, 1954.
47. H. E. Bent and C. L. French, J. Am. Chem. Soc., 63: 568-572 (1941).
48. C. D. Hodgman, editor, "Handbook of Chemistry and Physics," 27th ed., p. 2210, Chemical Rubber Publishing Co., Cleveland, Ohio, 1943.
49. M. G. Mellon, editor, "Analytical Absorption Spectroscopy," p. 307, John Wiley & Sons, Inc., New York, 1950.
50. "Gmelins Handbuch der anorganischen Chemie," System No. 12, Polonium und Isotope, pp. 69-92, Verlag Chemie, G.m.b.H., Berlin, 1941.
51. O. Erbacher, Z. physik. Chem., A156: 135-149 (1931).
52. R. J. Prestwood, Polonium Extraction Using a Platinum Electrode and Hydrogen, Report AECD-2839, Apr. 10, 1944.
53. W. R. Kanne, Phys. Rev., 52(2): 380 (1937).
54. O. Erbacher, Z. physik. Chem., A165: 421-426 (1933).
55. M. M. Haring, Polarization Studies, Information Report No. 22, Report MLM-M-863, Jan. 22, 1945.
56. W. H. Power, Quarterly Progress Report, Report MLM-368-1, April, May, and June 1949, p. 62.
57. W. H. Power, Quarterly Progress Report, Report MLM-379-1, July, August, and September 1949, p. 82.
58. F. Joliot, J. chim. phys., 27: 119-162 (1930).
59. C. E. Shoemaker, private communication, Nov. 12, 1953.
60. J. H. Payne and G. D. Nelson, Quarterly Progress Report, Report MLM-828, Mar. 31, 1953, p. 17.
61. L. G. Fauble, Progress Report, Report MLM-M-250, Sept. 1–15, 1947.
62. R. E. Brocklehurst and L. F. Vassamillet, Progress Report, Report MLM-M-237, Aug. 16–31, 1947.
63. R. E. Brocklehurst and L. F. Vassamillet, Progress Report, Report MLM-66, Mar. 1–31, 1948.
64. R. E. Brocklehurst and L. F. Vassamillet, Progress Report, Report MLM-113, May 1–31, 1948.
65. R. E. Brocklehurst and L. F. Vassamillet, Progress Report, Report MLM-132, June 1–30, 1948.
66. R. E. Brocklehurst and L. F. Vassamillet, Progress Report, Report MLM-221, Oct. 1–31, 1948.
67. J. M. Goode and D. L. Timma, Quarterly Progress Report, Report MLM-379-1, Oct. 1, 1949.
68. J. M. Goode, Quarterly Progress Report, Report MLM-405-2, Jan. 1, 1950.

69. J. M. Goode, Quarterly Progress Report, Report MLM-484-1, Sept. 11, 1950.
70. J. M. Goode, Quarterly Progress Report, Report MLM-509, Dec. 4, 1950.
71. J. M. Goode, Quarterly Progress Report, Report MLM-535, Feb. 26, 1951.
72. W. G. Witteman and G. N. Spillert, Final Report, Report LA-1546, May 1953.
73. Progress Report Excerpts, Report WASH-82, Aug. 20, 1952.
74. Progress Report Excerpts, Report WASH-130, Jan. 20, 1953.

Chapter 5

BIOLOGICAL RESEARCH RELATED TO POLONIUM

By Edward Spoerl and David S. Anthony

INTRODUCTION

It became apparent, early in the work with Po^{210}, that the health hazard was one of the main considerations affecting the use of polonium. Knowledge of the hazard from polonium was limited to some acute-toxicity and metabolism information obtained at the University of Rochester.[1] A biological research program was established at Mound Laboratory to fill in the gaps in the information on polonium toxicity and metabolism.

This chapter is a report of that polonium biological research which was directly related to the purification of polonium for the preparation of neutron and alpha sources. The chapter is divided into two parts. Part A is essentially a summary of the more important effects of polonium. There is a minimum of technical detail in this part because it is intended to give only the over-all picture of polonium toxicity. Part B gives some technical detail of experiments or results which yielded the data for Part A.

PART A. MAJOR POLONIUM EFFECTS

The effects of polonium were determined in experimental animals, chiefly the rat. The results are summarized in Table 5.1.

The LD_{50} (the dose lethal to 50 per cent of a population) at 20 days was determined for the cat, dog, rabbit, mouse, and rat, following a single injection of the polonium directly into a suitable vein. Since the rat was the species most sensitive to polonium in these 20-day tests, it seemed to be the best animal to use for further studies designed to yield a conservative determination of the largest dose of polonium which could be tolerated without any measurable effect. In actual practice, each succeeding experiment employed successively lower dose levels. Thus a gradation of effects from severe through mild to

Table 5.1 — Summary of Effects of Polonium on Experimental Animals

		Usual effects			
μc/kg of body weight	Animal	Lethal	Histopathological	Hematological	Gross
			Single Dose, Intravenous Injection		
50–100	Cat, dog, rabbit, mouse	LD_{50}, 20 days, about 80 μc/kg	Generalized massive tissue destruction	In rapid succession, severe loss of lymphocytes, all white blood cells, red blood cells, and hemoglobin	Complete loss of appetite; rapid weight loss, lethargy, death
35–45	Rat	LD_{50}, 20 days, about 40 μc/kg	Same as described above for other species at higher doses		
10–30	Rat	LD_{50}, about 50 to 250 days	In animals living 100 days or more, rapidly developing kidney damage	Moderate to severe early loss of white blood cells, later recovery, still later relapse; effects on red blood cells and hemoglobin only as rat is dying	Some early loss of appetite; moderate to severe weight loss
1–10	Rat	LD_{50}, about 300 to 500 days	Virtually every rat slowly developed kidney damage; some showed injury to the heart	Transient reduction of white blood cells at early time followed by recovery	Moderate weight reductions at higher dose levels
0.5–1.0	Rat	Reduction of life span by 10 to 20% in males only	Occasional mild kidney and/or thyroid lesions; otherwise no visible injury	No detectable hematological effect	None
0.25	Rat	None (i.e., the time required for ½ the population to die was ~600 days)	None	None	None

Table 5.1 — (Continued)

		Usual effects			
μc/kg of body weight	Animal	Lethal	Histopathological	Hematological	Gross
		Multiple Dose, Intravenous Injections			
2 Repeated 10 times at 2-week intervals	Rat	Quantitatively lethal in period 140 to 200 days	Lesions developed more rapidly than in the equivalent single-dose experiments; also, severe liver damage	White blood cells show a drop in count from 12,000 to 18,000 cells/cu mm at start, down to 2000 to 3000 count after 140 days; red blood cells show progressively more marked anemia from 7 to 7.5 to 2 million total count; there were no recovery phases	Only very slow weight gain after second injection; males from 275 to 420 g and females from 250 to 325 g at 140 days postinjection; loss of appetite, some diarrhea
0.01 Approximately maintained through life by monthly replacement injections	Rat	Indistinguishable from rats similarly injected with physiological saline containing no polonium			
		Gavage			
1300–2000	Rat	LD_{50}, 20 days	Massive tissue destruction with erosion of walls of gut; marked destruction of lymph nodes, spleen, etc.	Marked loss of red and white blood cells	Loss of appetite, weight loss, diarrhea, hemorrhage from anus and around nose

zero effect could be observed. The effect which was the most sensitive criterion of polonium injury was the shortening of life span. The lowest single dose of polonium causing a measurable shortening of life span was 0.5 μc per kilogram of body weight, equivalent to 35 μc in a 70-kg (155-lb) man. The lethal action of multiple doses or doses given by stomach tube (gavage) has been only partially explored in that a complete spectrum of doses has not been employed. Related work in this field which was completed at the University of Rochester[2] will complement the results given here. The lowest multiple dose which resulted in a maintained body burden of about 0.01 μc per kilogram of body weight was used to determine whether there is a margin of safety in maximum permissible concentration (MPC) values for humans now in use. The highest MPC in regular use for polonium (to our knowledge) is about 0.003 μc per kilogram of body weight maintained throughout life. The fact that a dose more than three times larger than this value in a sensitive species (rat) caused no damage that could be found after the most careful search gives confidence in the safety of this MPC.

Slightly larger doses were required to observe consistent histopathological effects, i.e., to determine the so-called "critical organ" by microscopic evidence of damage to tissues or organs. The kidney proved to be the critical organ at low dose levels in the single-dose experiment. With higher level multiple doses, however, severe liver damage, in addition to the kidney lesions, occurred. No liver injury was observed at any dose level in the single-dose series.

Hematological effects, i.e., effects on blood, especially on the kind or number of blood cells, were consistently observed only with polonium injections which were large enough to cut the life span approximately in half. This result strongly suggested that frequent periodic blood counts had no value as a method of monitoring exposure to polonium.

Gross changes in animals, such as loss of appetite, loss of body weight, and poor fur, occurred only at relatively high dose levels and thus constitute no reliable criteria of polonium damage. If gross changes appeared in a rat, its early death was a certainty.

It will be noted that Table 5.1 carries no reference whatever to cancer. One of the real surprises to the Mound Laboratory biologists was the complete lack of any evidence that polonium had any effect on cancer incidence in rats. This is not in agreement with limited data on mice obtained elsewhere.[3] No explanation of these findings has been advanced other than the observation that the very high normal cancer incidence of these Sprague-Dawley rats (>35 per cent of all control rats and of rats in the low single-dose experiments over 2 years of age) made impossible the observation of any small effect on cancer incidence.

PART B. EXPERIMENTAL RESULTS

1. TOXICITY STUDIES

1.1 *Acute and Subacute Toxicity in Rats and Mice.* The first experiments completed at Mound Laboratory were those to determine the 20-day LD_{50} for rats and mice. Studies of this type are usually considered necessary first steps in studies of the biological effects of an agent because they delimit the region of effectiveness and make possible the selection of appropriate doses.

The rats used were of the Sprague-Dawley strain, and from observations on splenectomized animals the rats used in the Mound Laboratory experiments appeared to be free of *Bartonella muris* infection. This freedom from *Bartonella* infection is important since some of the effects of polonium could not be evaluated in infected rats. Two groups of rats were injected intravenously (tail vein), and two groups were treated by gavage administration in which the injection solution was placed directly in the stomachs of the rats through a rubber tube swallowed by the animals.

The average 20-day LD_{50} for intravenously injected polonium was 43 μc per kilogram of body weight in male rats and 36 μc per kilogram of body weight in female rats.[4] These results were obtained on approximately 100 rats of each sex, divided into 11 dosage levels. Similar experiments with mice of the CFW strain gave LD_{50} values of 80 and 100 μc per kilogram of body weight, respectively, for the males and females following intravenous administration.

A semilog plot of the acute lethality in rats at other time periods is given in Fig. 5.1. The time scale in this figure is the number of days from injection until the death of the middle animal in the group (median lethal time). The rats were grouped irrespective of sex. Since they were usually injected when they were 100 to 140 days of age, the total age at death was at least 100 days more than the age shown in the figure. It can be seen that with doses from 70 to 30 μc per kilogram of body weight there was not much dependence of median lethal time on dose. However, with doses ranging from 30 to ~4 μc per kilogram of body weight, the median lethal time was strongly dependent on dose. The chronic lethality is discussed in detail in Sec. 1.3.

In the two gavage experiments with rats, nine or ten males and the same number of females were used for each of the eleven dosage levels. The average LD_{50} value for the males was 1650 ± 252 μc per kilogram of body weight, and for the females the value was 1325 μc per kilogram of body weight. [The estimation of the LD_{50} for female rats of both gavage experiments (1150 and 1500 μc) is based on so few points that this value must be considered a crude approximation.] The data obtained do not allow a statistical demonstration of the sex difference indicated.

1.2 *Acute Toxicity in Other Animals.* Because the aim of the biological research program was to establish human tolerance and toxicity values (to be obtained by extrapolation from animal studies), it was necessary to know something of the toxicity of polonium to several kinds of animals. In succeeding studies, dogs, cats, and rabbits were used in LD_{50} determinations. A group of 12 mongrel dogs was used, and the polonium was injected via the cephalic vein in the right foreleg.[5] A working figure obtained from the experiment for the LD_{50} value (20-day) was taken to be approximately 70 μc of polonium per kilogram of body weight. The general appearance of the dogs just prior to death was

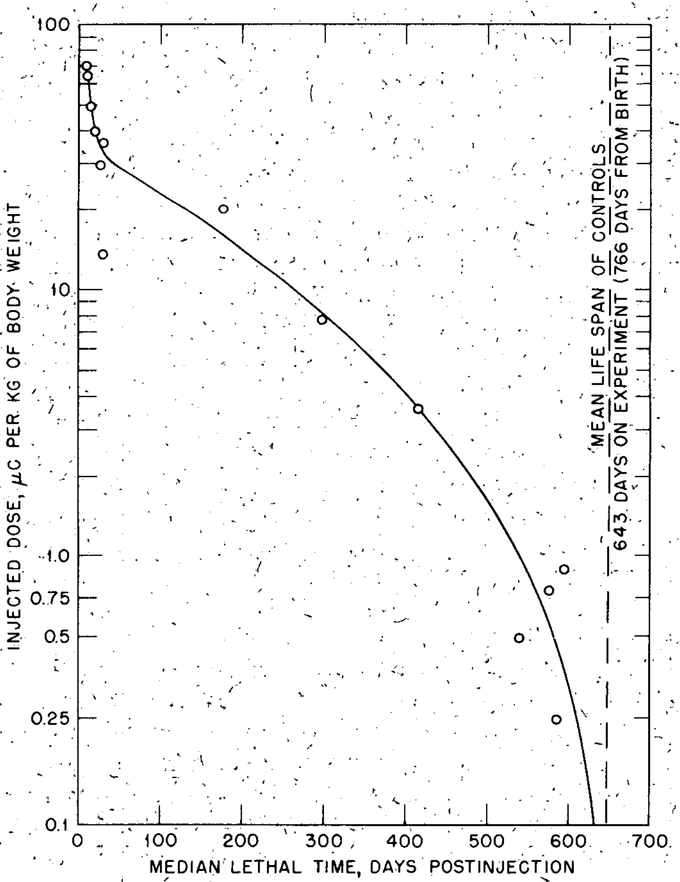


Fig. 5.1—Median lethal time vs. dose.

very similar. There was marked loss of hair, loss of body weight, lethargy, and lack of appetite. Ulcers of the skin developed and refused to heal. A group of 24 cats was used in a similar experiment.[6] The cats were injected via the saphenous (leg) vein. The 20-day LD_{50} value was determined to be 69 μc of polonium per kilogram of body weight. No very precise estimate of the toxic dose was made with rabbits, although the results obtained indicated that the 20-day LD_{50} for these animals would also be in the region of 70 μc per kilogram of body weight.

From the standpoint of polonium sensitivity (a sensitive animal species being preferable for extrapolation to humans), the rat proved to be an excellent choice for the bulk of the Mound Laboratory experimental biological work.

1.3 *Chronic Toxicity in Rats.* It was pointed out above that long-term or chronic studies are a direct way of measuring tolerance values for a given material. Studies of this type are still being carried out at Mound Laboratory. A series of experiments at doses of 1 to 8 μc per kilogram of body weight showed that even such relatively low single doses of polonium caused irreparable damage and early death in rats. That is, such doses were well above the lowest effective dose. Consequently an experiment was initiated to measure the long-term effects of still lower doses of polonium in an attempt to determine the lowest single dose which would measurably affect a significant fraction of a large group of rats.[7] The dosage levels used were 0 (control), 0.25, 0.50, and 0.75 μc per kilogram of body weight, and the criterion of effect was a shortening of life span, the rats being observed until they died. Eighty rats, 40 males and 40 females, were employed in each group. The effect of these doses on median lethal time (both sexes combined) can be seen in Fig. 5.1. Since such individual median values are not susceptible to statistical evaluation, the life-span data were used for statistical analysis. The most striking feature of the life-span data was the difference in longevity between males and females. Male rats showed a significant shortening in life span at the 0.50- and 0.75-μc dosage levels but not at the 0.25-μc level. Thus the lowest effective dose of polonium in the male rat was equal to or slightly less than 0.5 μc per kilogram of body weight. There was a much greater degree of variance in the data for the female rats, and only at the 0.75-μc level did it appear that some reduction (not clearly significant) in life span had occurred.

Studies of chronic toxicity resulting from a maintained very low body burden of polonium were also carried out. A body concentration of 0.01 μc per kilogram of body weight was maintained in rats by monthly replacement injections equal to the polonium lost by excretion and decay during the previous month. One hundred rats were injected with polonium and maintained until their death, with observations being made on life span, tumor incidence, and food and water consumption. After the death of these rats, a total body polonium analysis was made to determine actual body content. After 28 months, this experiment has failed to show any toxicity from a maintained body burden of 0.01 μc per kilogram of body weight. Only 9 per cent of the control and 11 per cent of the polonium-injected animals are still living; therefore, it is safe to conclude that the life span was unaffected by this level of polonium (and shortening of life span has proved in other experiments to be the most sensitive criterion of damage). Maximum permissible maintained body burden for polonium at higher dose levels is being compiled from experiments performed at the University of Rochester.[2]

From the preceding experiments it can be concluded that any dose in excess of 0.25 μc per kilogram of body weight (about 17.5 μc or 3.9×10^{-3} μg total dose for a standard man) may be a dangerous amount in a human, whereas a maximum permissible continuously maintained body burden of 0.003 μc of polonium has at least a modest margin of safety. These conclusions assume that humans metabolize polonium in a manner and at a rate similar to the rat. Section 4 will bear on this point.

Several types of tumors, including adenoma, fibroma, adenofibroma, adenocarcinoma, and scirrhous carcinoma, were observed in the rats as they grew old. However, it was found that the number of animals having tumors was independent of the dosage level for both sexes and that no difference between control and treated animals occurred. The really remarkable feature of the tumor data was the very high incidence of tumors in senescent Sprague-Dawley rats. Thirty-six per cent of the rats developed tumors, after approximately 2 years on experiment, and of these tumors 35 per cent were malignant in nature. All but one of the tumors observed involved mammary-gland tissue.

2. DISTRIBUTION OF POLONIUM

2.1 *Gross Distribution.* The distribution of polonium in the rat following gavage (stomach-tube) administration has been compared with that following intravenous (tail-vein) administration. Approximately 3 to 5 per cent of the gavage dose was absorbed from the gastrointestinal tract. Figures 5.2 to 5.5 show the polonium concentrations in representative tissues at various times after an absorbed (gavage) or injected dose of 14 μc per kilogram of body weight. The data in all figures include the loss of activity due to radioactive decay as well as excretion. Thus the area under the retention curves is equivalent to the true radiation dose.

The rate of excretion at early times was very much higher in the gavage animals than it was in those receiving their dose intravenously (Fig. 5.2). The high early excretion in the gavage animals resulted

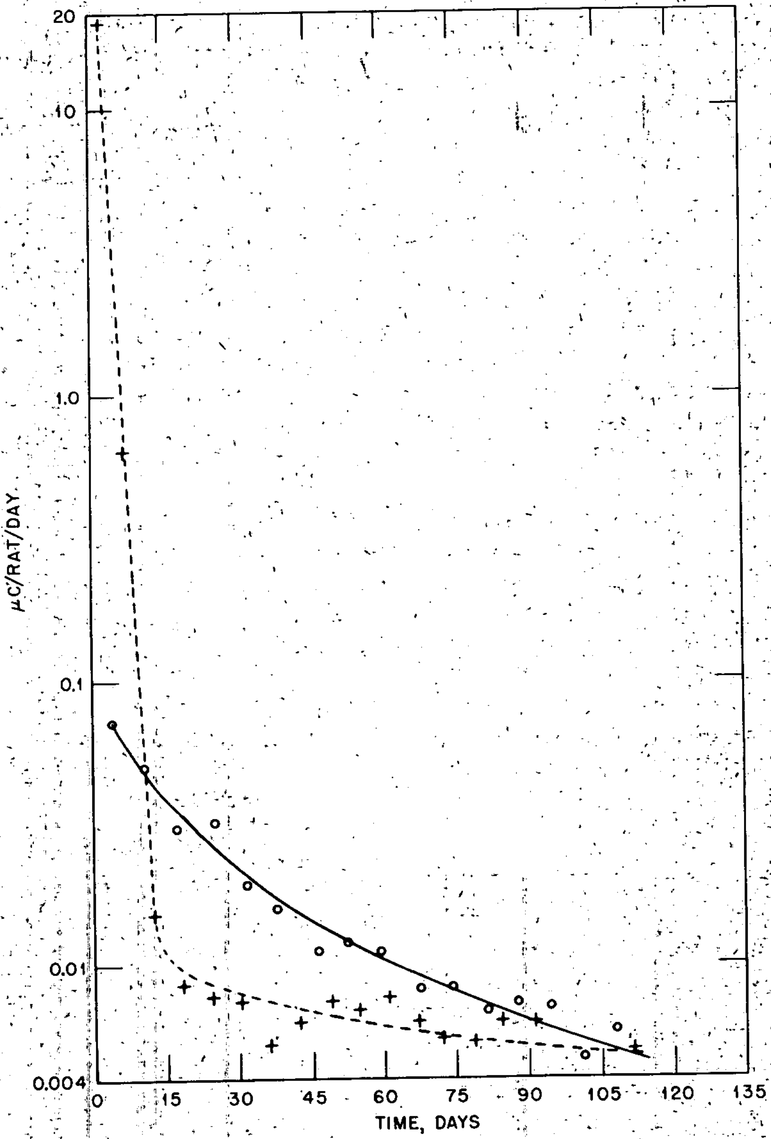


Fig. 5.2—Rate of excretion of polonium. ——, intravenous. -----, gavage.

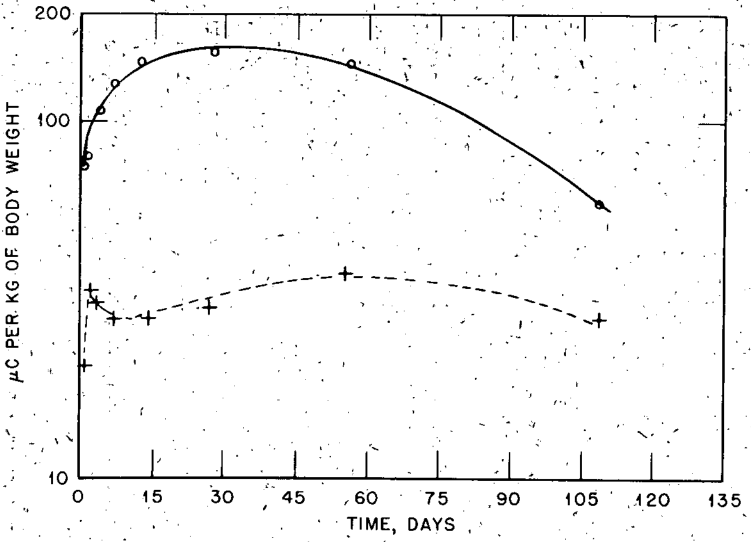


Fig. 5.3—Polonium concentration in kidneys. ——, intravenous. ----, gavage.

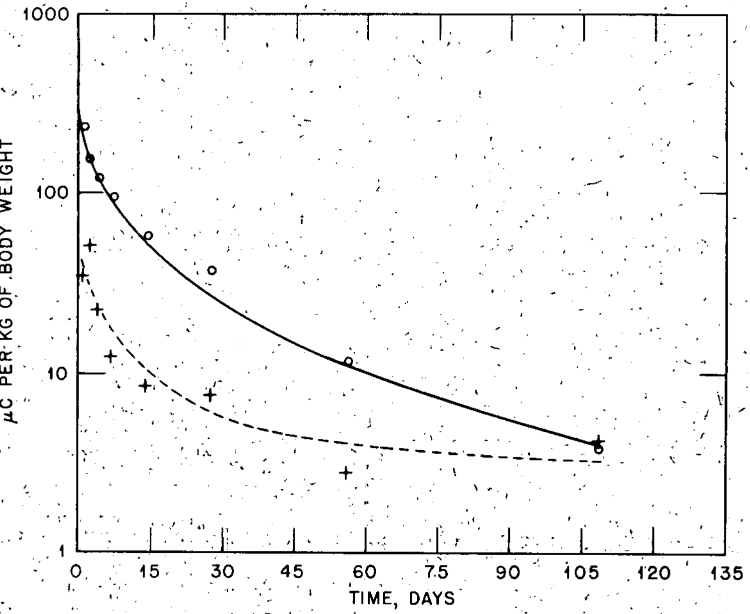


Fig. 5.4—Polonium concentration in liver. ——, intravenous. -----, gavage.

from voiding of large amounts of unabsorbed polonium. It was surprising that this effect continued for as long as 2 weeks.

The polonium concentration vs. time curves for two vital organs, the kidney and the liver, are given in Figs. 5.3 and 5.4. The pattern of polonium metabolism in the kidney differs sharply from that seen in the liver (and in other organs studied which are not further discussed here). A rise in polonium concentration with time occurred, and the concentration at all times was quite high. Thus the kidney was exposed to a much higher total radiation dose than, for example, was the liver, although the initial polonium concentration in the two organs was quite similar. This fact suggested that the kidney should be carefully examined for evidences of toxicity following single doses of polonium (see Sec. 3.2).

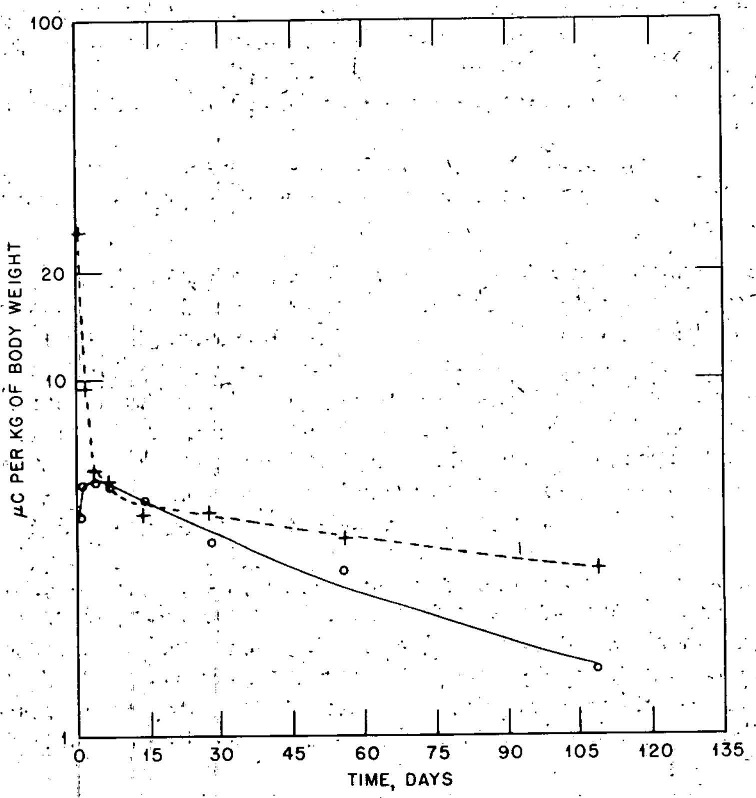


Fig. 5.5—Polonium concentration in carcass. ——, intravenous. ----, gavage.

The rate of loss of polonium from the carcass (Fig. 5.5) followed a course very similar to that seen in the liver after the first 2 weeks. That is, for a given method of administration, the slopes of the polonium concentration vs. time curves (Figs. 5.4 and 5.5) for the two tissues were virtually identical. Similar patterns were seen for other tissues where tissue atrophy was not a factor. For both tissues, the gavage animals lost polonium more slowly after the first few days than did the intravenously injected ones. It can be seen from these data that polonium is not one of the so-called "bone-seeking" radioelements. That is, it is not preferentially distributed to the bone nor is it tenaciously held there.

Polonium is primarily an irradiator of soft tissues or vital organs. Accordingly, it is in such tissues that one would expect to find evidences of damage.

2.2 *Detailed Study of Distribution Within the Blood: By J. E. Campbell.* The role of blood in the metabolism and toxicology of polonium has not been thoroughly investigated. However, certain observations made on polonium-intoxicated animals suggest the importance of blood in the polonium toxicity syndrome. Investigated were such factors as biliary excretion of polonium, the relatively high concentrations of polonium in the blood, and pathological alteration of several of the highly sensitive organs such as the spleen, bone marrow, and liver, which are closely associated with blood-cell storage, production, or destruction.

The purpose of the studies described below was to make a detailed investigation of the distribution of polonium in blood and to learn something of the chemical nature of the bond between polonium and blood. The work was done primarily with Sprague-Dawley rats, but all the critical experiments have been repeated on dogs with almost identical results. Observations are based on at least three, usually five, replicate experiments.

Centrifugal separation of polonium-containing blood into its major components revealed that 90 to 97 per cent of the polonium was in the red blood cells and that the remainder of the polonium was in both the plasma and the white blood cells. The blood was taken by cardiac puncture from rats which had been intravenously injected 4 days previously with approximately 50 μc of polonium per kilogram of body weight. Auxiliary experiments demonstrated that the techniques used in the separation, such as washing the cells with an isotonic solution of sodium chloride, had no effect on the distribution pattern obtained.

Experiments in which hemoglobin was carefully isolated by several different methods from polonium-containing red blood cells indicated that almost all the polonium was associated with the hemoglobin. Similar results have been obtained by Thomas[8] in studies in which polonium-containing blood was fractionated by means of silica-gel electrophoresis.

Chemical fractionation of lysed solutions of polonium-containing red blood cells by conventional methods into heme (insoluble acid hematin), globin (insoluble in dilute ammonium hydroxide), and the soluble residue revealed that almost all the polonium was associated with the globin fraction. However, an alternative method of fractionation in which the globin was removed in an acid-denatured form from acetone left the polonium in the soluble portion.

The correctness of the original observation that polonium is bound to the globin of the red blood cell has been indirectly confirmed in a series of in vitro polonium-uptake studies in which a lysed solution of red blood cells from normal rats and a nondenatured globin solution of equivalent concentration were found to have the same affinity for polonium. The experimental technique used in these studies was based on the competition for polonium by the sample and a neutral acid-charged ion-exchange resin, IR112 (Rohm & Haas Co., Philadelphia). In this system the amount of resin, polonium, and water, as well as the hydrogen-ion concentration and temperature, are held constant, and the end point of the procedure is the concentration of the sample necessary to bind 50 per cent of the polonium. It is important to note that no chemical treatment of the protein was necessary with this assay. Studies are now in progress using the ion-exchange technique to determine the functional groups in globin which bind polonium.

3. EFFECTS OF POLONIUM ON RATS

3.1 *Gross Effects.* The visible gross effects of single doses of injected polonium on rats were not dramatic until death was imminent. There was a loss of weight or a reduction of the rate of weight gain below that of the controls. The effect on weight was roughly proportional to dose. At late times the urine volume frequently exceeded water intake, although water intake often increased (to a lesser extent) terminally. In some rats hemorrhage around the eyes occurred as a terminal symptom. Also at late times the ears and eyes grew pale (indicating anemia), and the fur became rough and poor.

The animals receiving multiple injections showed much the same gross effects of the polonium as had the animals receiving single injections, with the exception of visible evidence of liver damage. Edema (swelling) of the face was the symptom of liver damage that was apparent upon external examination of the animals receiving multiple injections. The other gross effects appeared earlier, developed a little more rapidly, and became more severe than they did with equivalent single doses.

During the gavage distribution experiment the body weight of treated male and female rats dropped below that of the controls, i.e., weight increases in treated animals did not match the increases in control animals. The effect upon weight increases was more marked in the females. Food consumption and feces excretion in treated animals were less than for control animals, starting shortly after the beginning of the experiment and continuing to the termination of the experiment. The water-intake and urine-excretion patterns were different for treated male and female rats. Treated female animals consumed more water and excreted more urine throughout the experiment than did the control animals. Water intake and urine excretion in the treated male rats also were greater than in control rats for the first 3 weeks of the experiment, but after this period of time the treated male rats recovered to normal rates.

3.2 *Histopathological and Hematological Effects. By R. N. Cowden and R. E. Zipf.* A series of studies was carried out to determine histopathological and hematological (blood) changes in rats given a range of intravenous polonium doses such that changes during acute, subacute, and chronic toxicity could be observed. Dosage levels of 35, 23, 8, 3.6, and 0.9 μc of polonium per kilogram of body weight were used in these studies in which serial sacrifices of both polonium-injected and control rats were made at regular intervals.[9] Hematological studies consisted of erythrocyte (red-cell) counts, white-cell counts, differential white-cell counts, hemoglobin, hematocrit, and mean blood-cell diameter determinations. In addition, the effects of small repeated dosages of polonium have been studied in conjunction with metabolic studies.

The rats from these various injection levels were sacrificed through a period of time 375 days postinjection. Also, rats from 3.6- and 0.9-μc levels that were used for hematological studies were allowed to live past 375 days until they became moribund or died, at which times they were autopsied and sections were taken for study. Concurrently with these pathological studies, autoradiographic studies were done to follow the deposition of polonium in various organs at various time intervals, and attempts were made to correlate polonium deposition with histopathological change.

The acute dose levels (35 and 23 μc) showed very early blood dyscrasias (disorders) that are described more fully below. Along with the early blood dyscrasias and attendant bone-marrow damage, there was marked atrophy (degeneration) and hypoplasia (less than normal number of cells) of the lymphoid tissue and gonads. The kidneys showed the first changes at approximately 100 days postinjection on all injection levels. The changes were progressive with marked tubular damage, atrophy, and fibrosis. There was a progressive degenerative change in the ovaries at all injection levels, and the testes showed regenerative changes at the 8-μc level and at the lesser dose levels. In rats at the 8-μc level there was a heart lesion at 300 days and later, which also appeared in the heart tissues of rats injected with lesser doses of polonium. A few of the rats of the chronic injection levels showed hyperplasia of the thyroid gland at late time intervals postinjection.

The multiple-dose studies showed many interesting parallels and digressions from the pathological changes seen in the single-dose studies. When comparison was made between rats receiving a single dose of polonium and those receiving the same total dose in a series of injections, the pathological changes appeared earlier in the multiple-dose animals, were more marked, and involved organs not markedly affected in single-dose studies. In the multiple-dose experiments the kidney lesions described for the single-dose studies occurred earlier and progressed more rapidly, and the gonads and lymphoid tissue showed earlier and more profound change. The most striking difference noted between the single- and multiple-dose studies, when equal total amounts of polonium were given, was in the liver. This organ in the case of a single dose showed minimal changes. However, the multiple-dose studies showed several evidences of extremely severe liver damage (hyperplasia of bile-duct epithelium with fatty degeneration and fibrosis and necrosis of the liver-cord cells). These pathological studies of the effects of multiple doses of polonium were done in conjunction with the distribution studies described previously and showed a more rapid and pronounced toxemia accompanying the increased body burden of polonium.

The hematological studies were made on animals from the experiments set up for histopathological observations and consisted of complete peripheral blood surveys as well as some bone-marrow studies. In general, the picture seen was one of early severe blood damage at high dose levels; later, less severe damage at intermediate dose levels; and either long delayed, slight damage or no damage at all at low dose levels.

Blood dyscrasias were pronounced on the acute dosage levels (35 and 23 μc). The leucocyte counts showed a precipitous drop to very low levels by 24 hr postinjection, followed by slow recovery and then terminal leucopenia (low white-blood-cell count) as the animals became moribund. The total erythrocyte count took a pronounced drop at the 35-μc level at 21 days and at the 23-μc level at 40 days postinjection. There was only a partial recovery followed by marked anemias as the animals became moribund. The hemoglobin and hematocrit values somewhat paralleled the changes reflected in the erythrocyte counts. The red-blood-cell diameters revealed some enlarging of the cells.

The 8-μc level showed almost normal erythrocyte values until 180 days postinjection, when there was a precipitous drop to levels under 2 million cells/cu mm by 300 days. The hematocrit and hemoglobin values paralleled those of the erythrocytes at this injection level. The mean leucocyte counts showed the same early leucopenia observed at the higher dosage levels with almost complete recovery and then a marked leucopenia in the female rats from 260 to 300 days postinjection. In all these cases the lymphocytes showed a far greater reduction in total values than did the polymorphonuclear leucocytes. Thus the blood counts would show a relative increase in the leucocytes.

The hematological studies following chronic doses of polonium (3.6- and 0.9-μc levels) showed no changes through 375 days postinjection. The 0.9-μc level never showed any changes, although the 3.6-μc level showed a latent anemia and leucopenia.

Bone-marrow studies on rats injected with acute doses of polonium revealed severe damage (hemorrhage, fat replacement of marrow cells, and nuclear abnormalities in cells of the erythrocytic series during the first 2 weeks postinjection). At 3 to 6 weeks postinjection there was a severe loss of cells in the bone marrow with localized areas of cellular regeneration in the bone shaft. There was an abnormal maturation of cells. At 8 to 12 weeks postinjection there was cellular regeneration in the ends of the long bones with hypoplasia in the shaft marrow and fibrous replacement of the fat cells. At later times on these high doses some degree of recovery was noted, although abundant evidence of damage persisted.

At the intermediate dose level of 8 μc the bone marrow showed hemorrhages with a slight early hypoplasia which persisted and grew slightly more severe with time. From 84 to 302 days postinjection there was a moderate hypoplasia of the erythroblasts and normoblasts in the diaphysis with slight fibrosis.

At the low dose level of 3.6 μc there were no early signs of damage to the marrow, and the only late changes (after 375 days) were hyperplastic marrow with anemia and leucopenic values in the peripheral blood. The anomaly of more than normally cellular marrow with less than normally cellular peripheral blood is attributed to a hypersplenic response of unknown origin. The spleen was destroying the circulating cells faster than the marrow could make them.

The blood picture is being followed in rats that have been given very low doses of polonium both singly and in multiples, but no changes have been seen in over a year postinjection.

3.3 *Breeding and Oestrus-cycle Effects. By R. K. Davis.* The wide distribution of polonium in the body and the widespread histopathological changes caused by sufficient concentrations of this element imply that reproductive functions will be affected. Early data indicated that polonium caused the female reproductive system to maintain long periods of oestrus and in the male it caused a diminution in the number of spermatozoa. Two groups of 30 male, and two groups of 30 female, Sprague-Dawley rats were used in a breeding experiment[10] in which one group of males and one group of females were injected via the caudal (tail) vein with 14 μc of polonium per kilogram of body weight. Three days after injection the following mating crosses were made: (1) injected females mated with injected males, (2) injected females mated with control males, (3) control females mated with injected males, and (4) control females mated with control males. Matings in which injected males were used had significantly longer periods of gestation than other matings. This suggests that gestation per se was not extended but that insemination of the ova was delayed after the formation of the copulation plug. All matings produced about the same number of living young. However, the number of stillborn offspring increased significantly when one or both of the parents had been injected with polonium. This situation reflects the observation that injected females produced larger litters and suggests that the polonium produced an increased ovulation but prevented normal gestation of the increased number of fetuses. Analysis of the offspring for polonium content showed none to be present, indicating that little or no polonium crossed the fetal membranes and that the observed effect on mortality was due to an effect upon the pregnant females rather than a direct effect upon the young. In another experiment to evaluate polonium effects upon the oestrus cycle,[11] three groups (20 each) of young adult female Sprague-Dawley rats were injected via the caudal vein with 9, 20, and 30 μc of polonium per kilogram of body weight, respectively. Daily vaginal lavage smears were taken and read over an observational period of 154 days. All injected rats did not live throughout the experiment, and those that died were autopsied for urogenital system observations. It was concluded from the observations made that the early effect of polonium was to bring about the appearance of a prolonged early oestrus type of vaginal smear and that later, after the polonium had acted upon the urogenital system for a longer period, the early oestrus-type smear gave way to a dioestrus-type smear. The time required for the appearance of this series of events was related to the dosage of polonium. The surviving rats did not return to a completely normal oestrus cycle during the length of the experiment.

It is quite evident from these experiments that polonium affects the reproductive system of rats. The high dosage levels used result in many pathological changes, and, as a result, it is to be expected that interference with the reproductive systems would occur. Similar studies at low or chronic dosage levels would be of considerable interest in connection with human tolerance levels.

4. OBSERVATIONS ON HUMANS

The opportunity to observe toxic effects or metabolism of polonium in humans is quite restricted. Such observations are limited for the most part to cases in which accidental exposure has occurred. When accidents do occur, it is very worth while to observe the metabolism and other effects, if any, as completely as possible in an attempt to establish a relation between animal experimentation and human experience.

A calculation of the half life of polonium in humans has been made from the data obtained in routine urine analysis on Mound Laboratory personnel.[12] The calculation actually gives a half time for urinary excretion, i.e., the length of time required for the polonium excretion rate to decrease by one-half, but if it is assumed that such excretion provides an index of the amount of polonium in the body, then the calculation might be called a "derived effective half life." There is abundant evidence in the experimental data on animals that the excretion of polonium does bear a simple direct relation to the body burden. There is absolutely no evidence of the body burden becoming less (or more) available to excretion with time such as one sees in the case of radium and plutonium.[1]

The health physics urine-count records at Mound Laboratory were searched for instances of substantial amounts of excreted polonium, and cases were used in which the maximum recorded count per minute per 50-ml sample exceeded 100 (MPC is 500 dis/min/24-hr-sample). If it is assumed that excretion is exponential, a straight line may be fitted to the logarithm of the recorded counts by the method of least-squares analysis, and the half life may be taken from a graph of these data when plotted. The average half life obtained from the cases studied was 36.6 days. This compares closely with an average half life in rats of about 35 days. It should be noted that fitting curves to human data on polonium excretion is complicated by the very wide fluctuation in amount of excretion from day to day or sample to sample in a given individual. This fluctuation is a characteristic of polonium metabolism. The relation between human excretion and retention of polonium has not been completely evaluated.

REFERENCES

1. R. M. Fink, editor, "Biological Studies with Polonium, Radium, and Plutonium," National Nuclear Energy Series, Division VI, Volume 3, McGraw-Hill Book Company, Inc., New York, 1950.
2. J. N. Stannard, private communication, Apr. 14, 1954.

3. M. P. Finkel, W. P. Norris, W. E. Kisieleski, and G. M. Hirsch, The Toxicity of Po^{210} in Mice, I, The 30-day LD_{50}, Retention, and Distribution, Report AECU-2176, June 1952.
4. R. K. Davis, The LD_{50} (20 Days) of Polonium, Report MLM-474, June 19, 1950.
5. R. K. Davis and W. P. Jolley, Twenty-day LD_{50} Determinations for Different Species of Laboratory Animals, I, Studies on Dogs, Report MLM-552, Apr. 23, 1951, p. 17.
6. R. K. Davis, W. P. Jolley, and C. Lizardi, Twenty-day LD_{50} Polonium Determinations for Different Species of Laboratory Animals, III, Studies on Cats, Report MLM-648, Jan. 21, 1952, p. 33.
7. R. K. Davis and G. T. Stevenson, Quarterly Progress Report, Report MLM-952, Mar. 10, 1954, p. 4.
8. R. Thomas, private communication, Oct. 15, 1953.
9. R. N. Cowden, Histopathological Study of Sprague-Dawley Rats Injected Intravenously with Varying Amounts of Polonium, Report MLM-761, Apr. 1, 1952.
10. R. K. Davis, W. P. Jolley, and J. J. Weitz, Quarterly Progress Report, Report MLM-407, Jan. 1, 1950, pp. 9-14.
11. R. K. Davis and W. T. Rockhold, Quarterly Progress Report, Report MLM-493, Oct. 9, 1950, pp. 15-27.
12. E. S. Spoerl, Quarterly Progress Report, Report MLM-626, Oct. 22, 1951, p. 73.

Chapter 6

POLONIUM FROM LEAD RESIDUES

By Harvey V. Moyer

1. INTRODUCTION

The possibility of obtaining polonium from the irradiation of bismuth in a nuclear reactor was appreciated by those who organized the Dayton Project. However, by the time the Dayton Project was organized, no bismuth had been irradiated except in a cyclotron, and the uncertainty of obtaining polonium by means of a nuclear reactor appeared to justify setting up a process for obtaining polonium from natural sources. This chapter describes work conducted at the Dayton Project for the separation of polonium from lead residues.

2. COMPOSITION OF LEAD DIOXIDE AND ASSAY PROCEDURES

2.1 *Source of Lead Dioxide.* The raw material for the lead process was shipped to Dayton, Ohio, from Port Hope, Ontario, by the Eldorado Mining and Refining Company. A total of 73,774 lb (dry weight) was received and processed.[1] The lead dioxide was obtained from African and Canadian uranium ores from which uranium, radium, and silver had been extracted. The processing of the African ore varied somewhat from the operations applied to the Canadian ore. Since the African ore was not roasted, it was assumed that the lead dioxide from this source would be initially richer in polonium than the residues from Canadian ore. The processing of the Canadian pitchblende was described by Pochon[2] in 1937 and is shown in the flow sheet, Fig. 6.1. (In a conference at Port Hope, Ontario, on Dec. 22, 1943, Pochon suggested to Lum

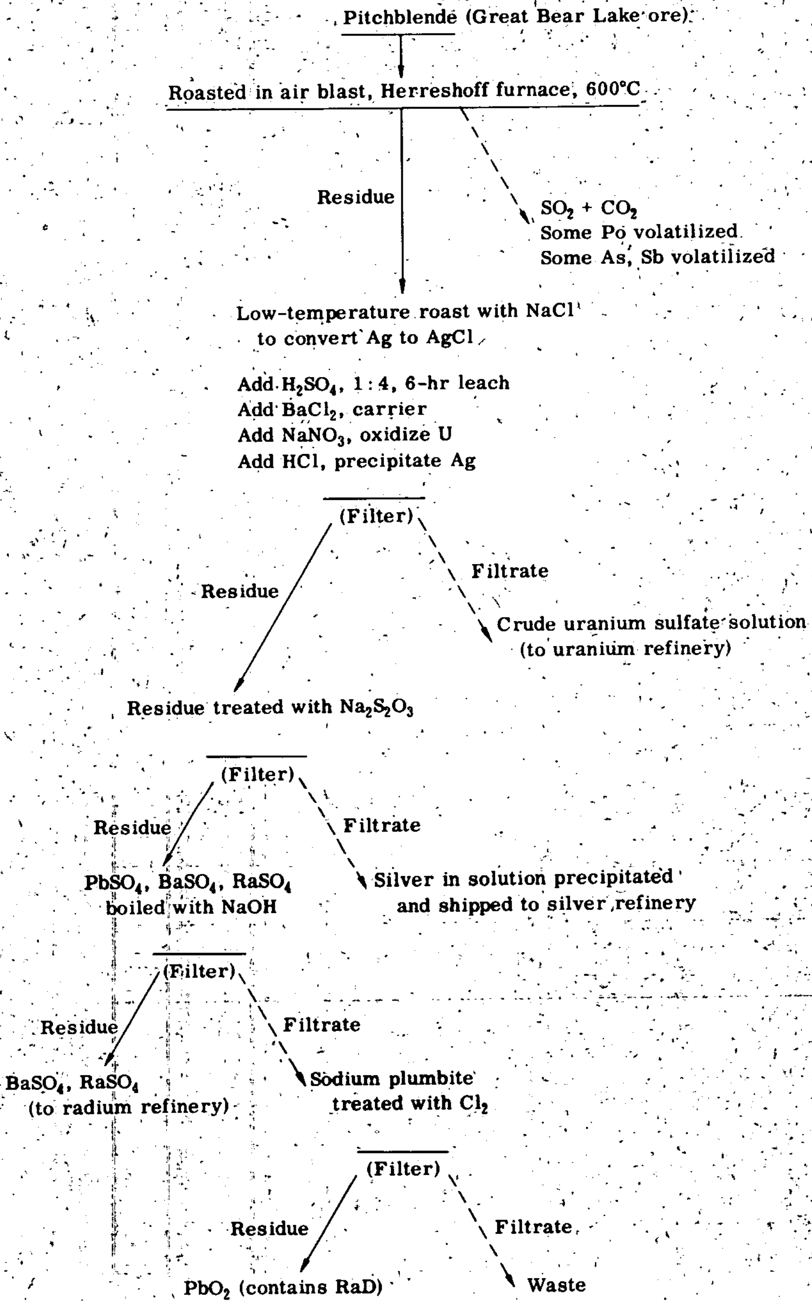


Fig. 6.1—Production of lead dioxide from pitchblende.

and Fernelius[3] that a sensitive calorimeter might be the best method of measuring high concentrations of polonium.)

2.2 *Analysis of Lead Dioxide.* The first shipment of 6250 lb of lead dioxide was received Nov. 10, 1943. It was largely African in origin but contained some material from Eldorado ores. Chemical analyses and qualitative spectrographic analyses showed that the lead dioxide contained many impurities in sufficient concentration to present difficulties in processing the material. This is shown in Table 6.1.

Table 6.1—Analysis of Lead Dioxide

Chemical analysis, %		Additional elements by spectrographic analysis	
Pb	81.13	Ba	Te
Fe_2O_3	1.25	Sb	Ag
Na_2O	0.70	V	Au
SiO_2	0.15	Bi	Pt
Mn	0.005	Al	Pd
Cl	Present	Mg	
Se	Present	Ni	
U	Present	Ca	

The impurities which were most important in the operations for separating polonium were iron, silicon, tellurium, selenium, and silver.

2.3 *Radioactive Assay of Lead Dioxide.* It was assumed that radioactive equilibrium had been reached between RaD and RaE in accordance with:

$$Pb^{210}(RaD) \xrightarrow[22\ yr]{\beta^-} Bi^{210}(RaE) \xrightarrow[5\ days]{\beta^-} Po^{210}(RaF) \xrightarrow[138.4\ days]{\alpha} Pb^{206}(RaG)$$

This assumption was justified since the lead dioxide was at least 60 days old when received in Dayton. The beta radiation which was counted came only from RaE, since the low-energy beta emission from RaD was not counted with the Lauritsen electroscope nor by the Geiger-Mueller counters which were used. The alpha radiation was measured in the early months of the project with a parallel-plate alpha counter. Results of the early assays varied considerably because of the low solubility of the sample, adsorption on glass during transfers, and imperfect corrections for backscattering and coincident disintegrations. The following results were picked by Weimer[4] as the most probable minimum values for a composite sample prepared from portions taken from 20 bags at random in the first shipment:

2619 α dis/min/mg = 1.07 curies/ton

3280 β dis/min/mg = 1.34 curies/ton

The second shipment, which was received Jan. 10, 1944, consisted of four lots which came from ore processed at Port Hope during the months indicated in Table 6.2. Assay results are also indicated in Table 6.2. The alpha assay showed that the quantity of polonium in the different lots was fairly consistent with the age of the processed ore. The RaD content indicated that the maximum quantity of polonium which could be expected in 2 years would not exceed 2 curies per ton of lead dioxide.

Table 6.2 — Assay of Second Shipment of Lead Dioxide

Lot marked	Net wt., tons	Moisture, %	Electroscope, div/sec	RaD, curies/ton	Activity, dis/min/mg	Po, curies/ton
Sept.	3.0	4.09	1.235	2.29	2854	1.17
Oct.	3.55	3.88	1.136	2.11	2286	0.95
Nov.	1.55	5.43	0.936	1.74	1458	0.60
Dec.	4.54	4.11	1.143	2.12	842	0.35

2.4 *Assay Procedures for Polonium.* (a) *Thick-sample Techniques.* The first attempt at counting thick samples was made by placing finely ground and screened lead dioxide in a circular depression 0.5 in. deep and 0.025 in. in diameter which had been made in a piece of sheet platinum. Brass disks of similar design were later found to be more satisfactory than the platinum because they were less expensive and had less tendency to crinkle when handled. The dry material was pressed into the depression with a small spatula and counted directly in a parallel-plate alpha counter. The count was independent of the weight of material in the disk but dependent on the surface area exposed. Material of 100 to 200 mesh gave results reproducible within ±5 per cent.

Another method of thick-sample counting proved more reliable than the disk method and was less likely to contaminate the counting chamber. This method involved compressing the solid material into pellets $^3/_8$ in. in diameter and $^1/_8$ in. in thickness. Samples from all shipments were made into pellets and counted in a parallel-plate alpha counter by means of a specially built pellet holder. The alpha particles entered the counting chamber through a circular aperture in a diaphragm against which the pellet was held by slight pressure. This holder is shown in Fig. 6.2. Smaller apertures were used for samples of higher activity. Since only the activity of the surface of the pellet was measured, it was necessary to prepare pellets of known polonium content in order to obtain a factor relating the measured activity to the polonium content of the pellet. It was observed that the counts from a pellet were independent of the side counted and not affected by rotating the pellet.

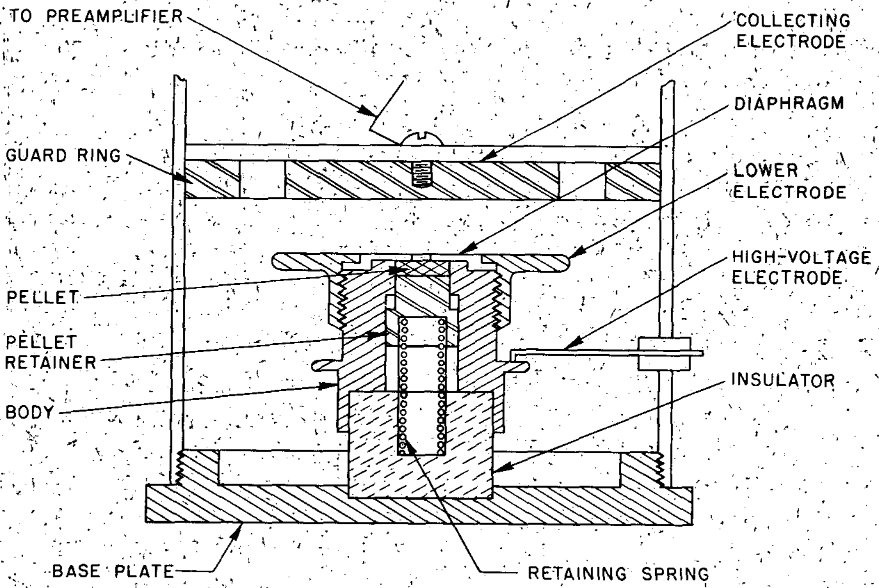


Fig. 6.2—Pellet holder.

(b) *Thermal Volatilization.* The thermal volatilization method depended upon volatilizing the polonium from a solid sample. It was used successfully on both natural and synthetic samples of lead dioxide. A weighed sample was put in a porcelain boat which was placed in a quartz combustion tube and heated to 650°C in the presence of sulfur dioxide. The lead dioxide was thereby converted to lead sulfate which was less fusible than the dioxide in the presence of the impurities in the sample. Results were low if the sample fused during the distillation of the polonium. The polonium was volatilized at 850 to 900°C *in vacuo* and collected outside the furnace in the cooler part of the combustion tube. The distilled polonium was washed out with concentrated nitric acid and diluted to a known volume, and an aliquot was counted. Results were usually consistent within ±3 per cent. The principal disadvantage of the method was that it was tedious and time-consuming. It served principally as an independent means of checking the accuracy of other methods.

(c) *Solution Method.* One-gram samples of solid material were weighed, and each was transferred directly into a 100-ml volumetric flask. To each flask was added 70 ml of concentrated hydrochloric acid. After being vigorously shaken, the mixture was allowed to stand for 15 min and was then diluted to the mark. A 10-μl sample was placed on a glass slide, dried, and counted. The same procedure was used in preparing samples for beta counting in the assay of material for RaD content.

2.5 *Lauritsen Electroscope for Beta Assay Procedures.* A thick sample was prepared by pressing the lead dioxide with a special plunger into a shallow box, 27 by 27 by 10 mm, in such a manner as to leave a smooth surface always the same distance from the aluminum window of the electroscope. The electroscope was calibrated with an active sample of lead dioxide which had been assayed by R. J. Prestwood of Los Alamos Scientific Laboratory by a method involving the chemical separation of RaE (Bi^{210}) from the sample.

2.6 *Growth of Polonium as a Measure of RaD.* The lead dioxide, when received in Dayton, had aged only a few months from the time of its preparation at the Port Hope refinery. Alpha and beta assays indicated that the polonium content of the lead dioxide was derived entirely from the decay of the RaD in the material. It was possible, therefore, to determine RaD by measuring the increase in polonium in the same sample over a known period of time. The pellets prepared from each shipment of lead dioxide were convenient samples for this determination. The calculation of the quantity of RaD from the increase in RaF is based on a solution of the equation

$$\frac{dN_F}{dt} = \lambda_D N_D - \lambda_F N_F$$

where N_F and N_D are numbers of atoms of RaF and RaD, respectively, and λ_D and λ_F are the respective disintegration constants. It was assumed that RaD remained essentially constant during the 96 days between measurements and that RaE could be neglected since it was in equilibrium with RaD. The RaD content of various shipments of lead dioxide is shown in Table 6.3.

2.7 *Alpha and Beta Assaying During Processing.* Frequent assaying of solutions was necessary during the processing operations. The most successful technique involved the spontaneous deposition of polonium on silver or nickel foil. Pieces of silver or nickel foil about ¾ in. square were cut and then washed with acetone. A background count before use was recommended. A 10-μl sample was transferred to the foil, and, if nickel was used, the sample was treated with 10 μl of 0.1N hydrochloric acid or glacial acetic acid. If silver foil was used, 10 μl of 1.0N hydrochloric or glacial acetic acid was used. The foils were allowed to stand for 30 min over water to prevent evaporation and were then washed with distilled water, dried, and counted. It was observed that filtration of the lead nitrate solutions through paper or by centrifugation reduced the count unless the acidity was greater than pH 1.5.

Table 6.3—RaD Content of Various Shipments of Lead Dioxide

Sample designation	Counts/unit time on June 10, 1944	Counts/unit time on Sept. 14, 1944	RaD, curies/ton (aging method)	RaD, curies/ton (electroscope†)
S-2-1	4060	4860	2.47	2.31
S-2-2	3977	4480	2.13	2.15
S-2-3	2750	3404	1.79	1.76
S-2-4	3158	4098	2.26	2.19
Aug.	3822	4480	2.22	2.18
Oct.	2556	2745	1.16	
Nov.	2735	2825	1.19	1.26
Jan.	2866	3730	2.05	
Feb.	2290	3405	2.10	

† Calibrated with sample assayed by R. J. Prestwood.

Beta assays of the lead nitrate solutions were made by placing 10-μl samples on glass, evaporating to dryness, and counting.

The most consistent results in assaying insoluble residues were obtained by treating 0.1-g samples with 30 ml of 6N hydrochloric acid, heating for 15 min on the hot plate, diluting to 100 ml without filtration, and counting 10-μl samples after evaporation on glass slides.

3. DISSOLUTION OF THE LEAD DIOXIDE

3.1 *Treatment with Nitric Acid and Hydrogen Peroxide.* The dissolution process began by grinding and screening the lead dioxide. The solid material which passed through a 60-mesh screen was treated in a 500-gal Pfaudler reaction vessel with water, nitric acid, and hydrogen peroxide. The water was run into the reactor, and the solid material was added and thoroughly mixed. The heat generated during the addition of nitric acid and hydrogen peroxide was removed by running water through the cooling jacket of the reactor.

The acid and peroxide were added at such a rate that the temperature did not rise above 40°C because above this temperature the decomposition of hydrogen peroxide was excessive. The reaction of lead dioxide with hydrogen peroxide in the presence of nitric acid is

$$PbO_2 + H_2O_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + O_2 + 2H_2O$$

The last 10 per cent of the hydrogen peroxide was in excess of the theoretical requirement and was added at a slow rate while the mixture was heated slowly to 95°C. The temperature was kept at 95°C for 1 hr; then the mixture was cooled to 70°C and forced into a cone-bottom settling tank. The pH of the solution on cooling was 0.8 to 1.0. In early operations 12 to 24 hr was allowed for settling. Spectacular improvement in settling occurred in several difficult cases by adding 100 to 500 g of hot glue dissolved in 1 gal of water. (The addition of glue was a suggestion by M. M. Haring. Apparently this is an example of the coagulation of colloidal particles by the "sensitization" effect of nonelectrolytes.[5]) Solutions which had not settled on standing 36 hr gave crystal clear supernatant solutions in 2 hr after the addition of glue. In later operations a more satisfactory solution to the problem was the addition of lead carbonate to the original reaction mixture before the first filtration.

3.2 *"Cleanup" Operation.* The addition of a slurry of basic lead carbonate, which was prepared later in the process from wash solutions containing lead, served to precipitate iron and aluminum by raising the pH to approximately 4. In the early procedures this cleanup operation followed the first filtration, but it was found that settling was more rapid and one filtration was eliminated by adding the lead carbonate to the original reaction mixture. Eighty pounds of lead carbonate slurry was required for each batch of 1200 lb of lead dioxide. The addition was made in the original Pfaudler reactor by returning the suspension from a temporary tank. The reaction mixture was heated to about 95°C for 1 hr, cooled to 70°C, and finally forced into settling tanks. The residue was removed in stoneware filters. The supernatant liquid in the settling tank and the filtrate from the cleanup filtration were filtered through a small Sparkler filter (Sparkler Manufacturing Company, Mundelein, Ill.). The filtered solutions of lead nitrate were run into 3000-gal glass-lined storage tanks for aging.

3.3 *Filtration Problems.* Approximately 75 per cent of the digestion mixture could be removed in a normal run as a fairly clear supernatant solution. The remaining portion was charged into two 50-gal stoneware filters equipped with glass filter cloth in a metal screen basket. Filtration time varied from 16 to 24 hr per filter. The siliceous residue was washed twice with dilute nitric acid to remove soluble lead salts and twice with water. Effective washing required stirring the residue to prevent channeling. A filter aid (Dicalite 4200, Johns-Manville) was used to coat the final filter cloth before use. Dicalite 4200 was also added to the slurry in the ratio of 1 lb of filter aid to 2 lb of estimated solid material. The residue in the final filters was stored in 1000-gal wooden tanks equipped with agitator blades which could be used to stir the solid material into a slurry for removal through Saran or porcelain lines.

3.4 *Storage of Lead Nitrate Solutions.* The lead nitrate solutions were stored in nine 3000-gal glass-lined tanks. Each tank contained approximately 6000 lb of lead. The total quantity of radioactive lead in 28,440 gal of lead nitrate solution on May 15, 1945, was close to 67 curies, or nearly 0.9 g of Pb^{210}. This 0.9 g of RaD was the source of the polonium which it was proposed to remove every 60 days by a milking process which began with the coprecipitation of the polonium with bismuth as bismuth oxychloride.

A reduction in the polonium content in the lead nitrate solutions after 6 months aging to approximately one-half the calculated value was due to the formation of crystals of basic lead nitrate which were present in varying quantities in every tank. The sediment varied in composition in different tanks but contained an average of approximately 50 per cent lead and about 8 per cent silica. An alpha assay of the precipitate indicated roughly 50 μc of polonium per kilogram of sediment. It was assumed that the slow settling of the hydrated silica carried down a considerable fraction of the polonium after the solutions were air-stirred. A brief study of the sediment in the storage tanks was made in June 1945, but it was not completed because at that time sufficient irradiated bismuth was being received, and it was decided to discontinue the lead process.

4. CONVERSION OF LEAD CHLORIDE TO LEAD NITRATE

The lead chloride which had been prepared in the attempt to obtain polonium by the Dillon process (Chap. 1, Sec. 3) was converted to lead nitrate by a special process which began by treating the lead chloride with soda ash to form basic lead carbonate. The original lead chloride solutions had been evaporated to a wet cake which consisted of lead chloride crystals contaminated with copper and nickel salts as well as with the acid-insoluble material from the original conversion of lead dioxide to lead chloride. It was desired to obtain a concentrated lead nitrate solution which would be essentially free of copper, nickel, and chloride. About $5\frac{1}{2}$ tons of the lead chloride residues were processed.

The process consisted of the following five principal steps:[6]

1. The lead chloride was suspended in water, and the free hydrochloric acid was neutralized with ammonium hydroxide which also served to hold copper and nickel in solution.
2. The solution was treated with soda ash to form basic lead carbonate.
3. The basic lead carbonate was washed with water to remove copper, nickel, and soluble chlorides.
4. The lead carbonate was treated with water and nitric acid in the proper quantity to give a nearly saturated solution of lead nitrate.
5. The solution was adjusted to approximately pH 4.0 and stored for subsequent processing for polonium.

All five of these operations were completed in the same 500-gal Pfaudler glass-lined reaction vessel which was used for the dissolution of the lead dioxide. The reactor was first charged with 425 gal of water which was agitated and heated during the addition of a weighed quantity (approximately 1200 lb) of the semisolid lead chloride. A 100-ml aliquot was titrated with 1 : 5 ammonium hydroxide to an end point indicated by methyl orange. On the basis of the titration, ammonia solution was added to neutralize the free acid. While the heating of the reaction mixture continued, soda ash was added as rapidly as possible without allowing the pH to rise above 7.0 as indicated by frequent tests with indicator paper. After the temperature reached 80 to 90°C, soda ash was added slowly until the pH (determined with a pH meter) reached 8.1 to 8.4. The reaction was considered complete if, after 15 min heating, the pH did not fall below 8.1. Under these conditions the conversion to the basic carbonate was in excess of 99 per cent. The lead precipitate was washed in the reaction vessel until tests on the supernatant solution indicated that less than 0.01 per cent of the original chloride remained. The basic lead carbonate was then decomposed by adding concentrated nitric acid equivalent to the soda ash used. Special precautions were not necessary in this operation since no serious foaming resulted. The amount of acid was adjusted to bring the solution close to pH 1.0. After the nitric acid treatment the hot solution was treated with a slurry of basic lead carbonate to raise the pH to 4.0. The siliceous residue contained most of the iron and other impurities as well as practically all the polonium. The mixture was agitated for about 1 hr at 70°C and was then forced into a settling tank. The insoluble material settled readily and was finally removed by filtration. It was decided not to attempt to extract the polonium from the residue which was transferred to barrels for final disposal. The clear supernatant solution and the filtrate were filtered through the Sparkler filter and sent to storage. A total of 4275 gal of lead nitrate solution containing 7840 lb of lead was prepared by the process.

5. COPRECIPITATION OF POLONIUM WITH BISMUTH OXYCHLORIDE[7]

5.1 *Precipitation in Pilot-plant Operations.* Assays of the lead nitrate solutions indicated that 0.88 g, or approximately 67 curies, of radium-D was present in the entire 30,000 gal of solution. Calculations showed that approximately 10 curies of polonium per month should be formed after the solutions had aged for 60 days. It was proposed to set up a schedule whereby 500 gal of solution would be processed each day if the lead solutions should be needed as a source of polonium.

A process for milking the lead nitrate solutions for polonium was devised and operated through the pilot-plant stage. A total of 16 pilot-plant runs was made to test the procedure recommended by the research group. The pilot-plant operations began by charging a 50-gal glass-lined Pfaudler reaction vessel with 40 gal of aged lead nitrate solution. A wetting agent, approximately 0.01 per cent of the weight of the lead nitrate solution, was added to reduce adherence of the bismuth precipitate to the walls of the reactor. Span 20 (Atlas Powder Company) or Santomerse E (Monsanto Chemical Co.) was best for this purpose. Ammonium chloride and bismuth nitrate were added in equivalent quantities to form the bismuth precipitate with which the polonium coprecipitated. The ammonium chloride solution was added first and was followed by the slow addition of an equivalent quantity of bismuth nitrate solution. The bismuth solutions were prepared by dissolving 696 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 200 ml of 6N nitric acid and diluting to 1000 ml. Trial precipitations were made both at room temperature and at 95°C with digestion periods varying from 2 to 6 hr. A settling period of 18 hr was sufficient in most of the runs to produce a clear supernatant liquid. However, in some of the runs in which precipitation was made at higher pH and with less available bismuth, the precipitates were slow to settle and difficult to filter. The bismuth precipitate effectively removed the polonium from solution; even when the quantity of precipitate was reduced by one-half, the efficiency of removal was not reduced. Variations in the temperature, pH, and quantity of reagents chiefly affected the particle size of the precipitate. No difficulties were encountered in the transfer of slurries through valves or by means of Saran tubing.

5.2 *Treatment of the Bismuth Precipitate.* The precipitate which formed during the addition of bismuth nitrate was shown by analysis to be a mixture of $Bi(OH)_2NO_3$, $BiOCl$, $PbCl_2$ with approximately 0.2 per cent SiO_2, and small quantities of other elements including practically the entire polonium content of the solution. The washing of the precipitate was accomplished by digesting the precipitate for 30 min in the Pfaudler kettle at a temperature of from 80 to 85°C with each wash solution. The 0.1N nitric acid wash reduced the lead content to less than 1 per cent. The two digestions in 0.1N hydrochloric acid were made to convert the $Bi(OH)_2NO_3$ to BiOCl. Losses due to evaporation were replaced by the addition of water so that a constant volume in the Pfaudler reactor was maintained. The lead removed from the precipitate was recovered by treating the wash solution with sodium carbonate. The volume of the final residue from a single batch after washing was close to 3.5 liters. Analysis of the washed precipitate indicated 98 per cent BiOCl with 1 per cent lead and 0.1 per cent SiO_2. Only a trace of nitrate remained. Approximately 0.2 per cent of the activity was lost in washing the bismuth precipitate.

Several conclusions were reached regarding the practicability of removing polonium from active lead nitrate solutions through coprecipitation with bismuth oxychloride:

1. The polonium was efficiently removed from lead nitrate solutions by coprecipitation with bismuth oxychloride.
2. A suitable wetting agent was necessary to prevent the bismuth precipitate from adhering to the walls of the glass-lined reaction vessel and to aid filtration.
3. The bismuth precipitate after washing contained impurities sufficient to interfere with subsequent operations for the preparation of polonium.
4. Other possible methods for the removal of polonium from active nitrate solutions should be investigated.

No large-scale operations were conducted to recover polonium from the bismuth oxychloride precipitates. It was proposed,[8] in the event the processing of the lead chloride solutions should become necessary, to dissolve the precipitate of bismuth oxychloride in concentrated hydrochloric acid, dilute to the desired volume with 6N hydrochloric acid, and filter to remove silica. The filtrate should be treated with powdered metallic bismuth to precipitate the polonium. The further concentration of polonium might be accomplished by following nearly the same procedure as used for isolating polonium from irradiated bismuth.

6. EXPERIMENTS ON SEPARATING POLONIUM FROM LEAD NITRATE SOLUTIONS

6.1 *Reduction with Powdered Bismuth.*[9] The possibility of applying reduction with bismuth directly to the aged lead nitrate solutions was studied. A series of experiments was conducted in which 1900 ml of the lead nitrate solution in each test was treated under different conditions with powdered bismuth. Replacing the air with nitrogen and carbon dioxide caused no significant change in the rate of removal of activity from the solution. Washing the bismuth powder with hydrochloric acid prior to use did not change the rate of reduction. Reducing the particle size of the bismuth powder increased the rate of removal of activity. It was observed that a reduction with 325-mesh bismuth removed as much activity in 5 min as was removed in 1 hr with 150-mesh powder. Lowering the pH from 4 to 0.8 reduced the rate of reduction and increased the amount of bismuth which dissolved in the solution. Successive reductions with the same bismuth showed a significant reduction in the rate of removal of activity after the first run. This effect was more marked in an atmosphere of carbon dioxide than in air, probably because the increased amount of dissolved bismuth in the presence of air introduced the scavenging effect of precipitated bismuth compounds. A trial run with a 500-gal batch of lead nitrate solution was made in order to test the direct reduction procedure. The test was made in a 500-gal Pfaudler kettle and in the presence of air by treating the solution at pH 4 with a total of 6.0 kg of powdered bismuth (between 100 and 150 mesh) in three portions of 2.0 kg each. The first addition was made at the beginning of the run, the second after 60 min, and the third after 90 min of reduction. The removal of activity was measured throughout the operation by removing samples every 15 min.

Inconsistent results were obtained in the test samples unless suspended particles were removed either by settling or by centrifugation. The supernatant liquid from samples removed after 15 min of reduction time had lost nearly 98 per cent of its activity when allowed to settle for 48 hr. The results indicated that suspended material held a relatively large fraction of the polonium. After being agitated for $2\frac{1}{2}$ hr at room temperature, the bismuth powder was allowed to settle. The supernatant solution was returned to storage, and the bismuth powder was recovered by filtration, dissolved in 3 liters of aqua regia, and reduced again with 50 g of powdered bismuth. The bismuth recovered from the second reduction was analyzed spectrographically, and it contained gross amounts of silica and approximately 10 ppm each of silver, mercury, and gold. None of these elements was present in comparable amounts in the original bismuth. Assays of the original solution showed an initial activity of 267 mc, whereas the bismuth powder from the second reduction contained only 36.6 mc of polonium. Counting the hydrochloric acid wash solutions showed that nearly one-half the polonium was removable by washing with 1N hydrochloric acid. This was interpreted to mean that approximately one-half the polonium was adsorbed on suspended particles rather than reduced and deposited on the metallic bismuth.

The results of the experiments on the direct reduction of the lead nitrate solutions with bismuth metal indicated that the polonium which was removed was not deposited as metallic polonium on the surface of the bismuth but was carried down in some kind of scavenging action. The recovery of the polonium after the reduction procedure presented so many difficulties that further work on the method was abandoned.

6.2 *Reduction with Metallic Silver.* The spontaneous deposition of polonium on silver foil was well known by early investigators.[10–16] It was decided, therefore, to attempt the separation of polonium from the lead nitrate solutions by direct reduction with finely divided silver. Several tests were made in which 5 g of silver powder (80 or 230 mesh) was added to 1900 ml of aged lead nitrate solution at pH 4.0. Under the conditions of the experiment, pure silver was not efficient in removing the activity from the solution. Only about 60 per cent of the activity was removed in 60 min after rapid agitation in the presence of 230-mesh silver powder. In one experiment 50 per cent of the activity was removed in 5 min with silver which contained considerable silver oxide. In this test a white precipitate appeared in the solution, and therefore it was assumed that the polonium was removed by the scavenging action of silver chloride. As a result of this observation, silver chloride was tested as a concentrating agent, but it proved unsatisfactory because of difficulty in recovering the polonium from the precipitated silver chloride. The experiments with silver as a reducing agent led to the conclusion that some other procedure must be found. (A successful procedure[17] for removing polonium by spontaneous precipitation on silver strongly acid with hydrochloric acid was developed later. Early failures were due, in part at least, to insufficient acid in the polonium solution.)

6.3 *Reduction with Metallic Arsenic.* Powdered arsenic (5 g, 150 to 200 mesh) was tried as a reducing agent. The presence of air appeared to cause sufficient oxidation of the arsenic to bring about the precipitation of some compound of lead and arsenic. In the presence of air 99 per cent of the activity in 1900 ml of lead nitrate solution was removed in 10 min, but, when the air was replaced with carbon dioxide, complete removal of activity required approximately 1 hr. The rapid removal of polonium from the solution was assumed to be due to the scavenging effect of the lead-arsenic compound. In the absence of air no precipitate formed in the solution, and the rate of removal of activity indicated the deposition of polonium on the arsenic. Repeated washing of the arsenic with 6N hydrochloric acid failed to remove more than 65 per cent of the activity which had been carried down by the arsenic.

6.4 *Miscellaneous Scavenging Materials.* The coprecipitation of polonium with many different substances was well known to early workers. This property was observed by P. Curie and M. Curie[18] in their first paper on polonium. They reported that the first portion of precipitate which formed on diluting the bismuth nitrate solution contained the greater part of the activity. Experiments in this laboratory showed that a large number of scavenging agents were available but that the most difficult problem in the procedure was the recovery of the activity from the adsorbing or coprecipitating agent. Table 6.4 gives a summary of the results obtained with various materials.

Table 6.4—Removal of Polonium from 30 Per Cent Lead Nitrate Solutions by Various Scavenging Agents

Run No.	Material used	Per cent of activity removed in time indicated 5 min	15 min	30 min	60 min
48	PbO_2 (5.0 g)	93	96	97	98
49	Bismuth pyrogallate (5.0 g)	58	87	98	99
50	Antimony pyrogallate (5.0 g)	15	14	19	25
52	Activated carbon "Nuchar" (5.0 g)	98	98	99	99
53	Activated carbon "Norite" (5.0 g)	81	88	87	92
55	Alumina "Amphojel" (5.0 g)	53	45	83	76
43	Silica "Celite" (1.0 g)	22	24	24	27
46	Silica "Celite" (5.0 g)	47	45	39	32
60	Silica gel† lot 1 (2.5 g)	18	30	46	48
62	Silica gel lot 1 (1.0 g)	37		58	36
61	Silica gel‡ lot 3 (2.1 g)	12	22	48	33

† Silica gel prepared from $SiCl_4$ by hydrolyzing and drying at 350 to 400°C (80 to 170 mesh).

‡ Silica gel prepared from water glass by acidifying with HCl; drying, washing with NH_4OH, washing with H_2O, and drying at 130°C (80 to 170 mesh).

In each experiment 1900 ml of radioactive lead nitrate solution was stirred at 2200 rpm in a 3-liter flask in an air atmosphere. The initial count on the solution was 2764 counts/min/10 μl.

The most effective agents among those listed in Table 6.4 are lead dioxide, bismuth pyrogallate, and both forms of charcoal. However, in each case the difficulties in recovering the polonium from the reducing agent were such that further work with these materials was discontinued.

6.5 *Titanium Dioxide.* The most promising results in the study of adsorption methods for separating polonium from the lead nitrate solutions were obtained with powdered titanium dioxide. Considerable difficulty arose in the early experiments because of the tendency of titanium dioxide to float on the surface of the solution and to stick to the glass apparatus. This was overcome by the addition of 0.2 g of a wetting agent (Span 20) per liter of lead nitrate solution. Laboratory experiments indicated that the activity in the lead nitrate solutions was removed by contact with the titanium dioxide and that it could be quantitatively recovered by leaching with 6N or 3N hydrochloric acid. The activity was not removed in significant amounts by washing with water or with 3N or 6N nitric acid. In addition to small-scale laboratory experiments, tests were made in which the lead nitrate solution was passed through a filter bed of titanium dioxide. The filter bed was prepared by covering a coarse sintered-glass filter with asbestos fibers which effectively retained the particles of titanium dioxide. The results obtained by filtering 1000-ml lead nitrate solutions through such a filter bed are shown in Table 6.5.

Table 6.5—Removal of Polonium from Lead Nitrate Solutions at pH 4 by Filtration Through 15 g of TiO_2

Run No.	Filtering time, min	Activity removal,† %
1	45	99
2	37	98
3	38	98
4	37	97
5	45	94

† Total activity removed = 3.06×10^9 dis/min = 1.4 mc.

A quantitative recovery of the activity removed from the lead nitrate solution was obtained by leaching the titanium dioxide filter bed with either 6N or 3N hydrochloric acid. No attempt was made to separate the polonium from the hydrochloric acid solution. Although no large-scale experiments were attempted, the properties of titanium dioxide appeared favorable for such operations. In the presence of a suitable wetting agent the solid material settled readily, yet it could be handled as a slurry if necessary. The high melting point and low volatility of titanium dioxide suggested the possibility of removing the polonium by direct heating.

7. POLONIUM FROM SILICEOUS RESIDUES

7.1 *General.* The preparation of lead nitrate solutions containing RaD was the chief objective of the lead dioxide process. Many difficulties were encountered in this process, among which was the precipitation of polonium with siliceous residues. The recovery of polonium from these residues presented additional problems; however, practicable methods were developed for polonium recovery, although they could not be carried far enough to ensure a sufficiently high concentration of polonium-on-bismuth for efficient electroplating operations.

7.2 *Composition of Residues.* The insoluble material from the lead dioxide dissolution process was a complex mixture which contained about 90 per cent of the polonium content of the original lead dioxide. The residues contained hydrated silica and consequently were gelatinous in character and difficult to free from lead nitrate and other soluble salts. Certain residues which were analyzed contained 20 to 30 per cent lead. Spectrographic analyses showed that lead, iron, bismuth, and silica were present in highest concentration with magnesium, sodium, antimony, and vanadium present in appreciable amounts. Trace concentrations of aluminum, calcium, copper, germanium, mercury, silver, gold, platinum, palladium, uranium, arsenic, tellurium, and selenium were detected. The water content of the residue from the filters was roughly 70 per cent by weight.

The limited knowledge regarding the chemical properties of polonium made it impossible to know with certainty the form in which the polonium existed in the residues. However, the retention of the polonium by the residues was not surprising in view of the well-known tendency of polonium to coprecipitate with compounds of bismuth, lead, iron, aluminum, and many other elements. Experiments on the precipitation of polonium from the lead nitrate solutions showed that at pH 4 a wide variety of finely divided solids was effective in removing the element from solution. This is shown in Table 6.4.

7.3 *Experiments on Extracting Polonium from Residues.* A number of different acids and salts were tested for their effectiveness in extracting polonium from the siliceous residues. The preliminary tests were made by dissolving 0.5-g samples of a dry residue in 50-ml volumes of the reagents listed in Table 6.6. The dry residue from which the samples were taken was analyzed for polonium by the thermal volatilization method which is described in Sec. 2.4b. The samples were shaken 3 to 4 hr, and, after the solution had settled, the activity in the supernatant solution was determined. The effective reagents for extracting polonium from the residues were those which probably formed complex ions with the element. The halogen acids were so much more effective than nitric, sulfuric, or perchloric acid that the hydrogen-ion concentration did not appear to be the major factor in the extraction mechanism. Oxalic, tartaric, and citric acids were better extractives than the other organic acids tested but were less effective than the halogen acids. Negligible amounts of activity were removed by 0.01N, 0.1N, or 1.0N solutions of sodium hydroxide. Table 6.6 shows the results of experiments on the extraction of polonium with various reagents.

Table 6.6 — Extraction of Polonium from Siliceous Residues

Acids	Polonium extracted, %	Salts	Polonium extracted, %
Conc. hydrochloric	100	10% sodium oxalate	65
6N hydrochloric	94	4% ammonium bifluoride	53
6N hydrobromic	97	4% trisodium phosphate	16
Const. boil. hydriodic	90	5% sodium thiosulfate	5
5% oxalic	65	10% sodium tartrate	5
10% tartaric	35	5% ammonium salicylate	<1
4% citric	30	5% ammonium citrate	<1
6N nitric	9	5% ammonium acetate	<1
6N perchloric	2	5% sodium sulfamate	<1
6N sulfuric	2	5% sodium malonate	<1
6N acetic	1	5% sodium acetate	<1
Satd. salicylic	1 to 3	10% sodium sulfite	<1
10% sulfamic	1		
3% succinic	<1		
3% malonic	<1		
2% aspartic	<1		

Additional experiments were made with solutions of hydrochloric acid to show the effect of concentration of acid. It was found that 3N hydrochloric acid would remove at least 90 per cent of the activity, provided the residues were thoroughly agitated in contact with the acid. The acid treatment increased the gelatinous character of the residue; consequently difficult filtration, even with large amounts of filter aid, was indicated. Although the 3N acid was somewhat less effective in removing the activity than 6N acid, the weaker acid was selected for pilot-plant operations because of the corrosiveness of the stronger acid on contact with the stainless-steel equipment.

7.4 *Recovery of Polonium from Hydrochloric Acid Extractions.* The principal constituents in the hydrochloric acid extract were lead, nitric acid, and iron. The lead offered no difficulty in reduction with bismuth, but the nitric acid and ferric iron interfered. Powdered bismuth would not bring about the deposition of polonium because the bismuth dissolved in hydrochloric–nitric acid solution. Iron was a problem because metallic bismuth reduced ferric iron to the ferrous state before it would react with polonium.

It was possible to remove the nitric acid by the addition of formaldehyde and then to reduce the ferric iron by the addition of extrafine bismuth powder. After the removal of the nitric acid and the reduction of the iron, the polonium could be precipitated quite completely on 150- to 200-mesh bismuth powder.

7.5 *Hydrogen Sulfide Precipitation.* A separation of iron from polonium and bismuth was attempted by precipitation with hydrogen sulfide in hydrochloric acid solution. Experiments showed that polonium was precipitated by hydrogen sulfide in 1N hydrochloric acid but not in 3N or 6N solutions. Concentration of polonium by means of hydrogen sulfide precipitation was used by P. Curie and M. Curie in their earliest preparations.[19] It was found in this laboratory that, although polonium was quantitatively separated from iron by hydrogen sulfide precipitation, the handling of the precipitate in the available equipment and the subsequent recovery of the polonium were difficult.

8. THE TELLURIUM PROCESS[20]

8.1 *Introduction.* The concentration of polonium from the siliceous residues by direct reduction with powdered bismuth could not be carried far enough to ensure a sufficiently high ratio of polonium to bismuth for the final electroplating operation. Selenium and tellurium interfered with the deposition of polonium on small quantities of metallic bismuth because these elements were present in considerable concentration and coated the surface of the bismuth so completely that very little polonium was deposited. It was necessary, therefore, to remove the bulk of the selenium and tellurium before a second reduction with bismuth would be effective. Marckwald[21,22] was the first to precipitate tellurium and polonium together from a hydrochloric acid solution by means of the reducing action of stannous chloride. He also discovered that tellurium and polonium could be separated by use of hydrazinium chloride in proper concentration. The stannous chloride reduction step was used by Curie and Debierne[23] in the first relatively large-scale preparation of polonium from several tons of lead sulfate residues from pitchblende. Haissinsky and Guillot[24] reported that hydrazinium chloride reduced polonium to a lower oxidation state. Marckwald[12] reported that polonium was partially precipitated with selenium and tellurium if a solution of the elements in dilute hydrochloric acid was treated with sulfur dioxide. Karl,[25] on the other hand, reported that the polonium remained in solution when a warm hydrochloric acid solution of tellurium and polonium was reduced with sulfur dioxide. Results in this laboratory confirmed Karl's observations.

8.2 *Stannous Chloride Reduction of Tellurium and Polonium.* The success of the early workers in concentrating polonium by reduction with stannous chloride made this appear a logical step in the extraction of polonium from the siliceous residues. Preliminary experiments indicated that the bulk of the selenium and tellurium could be precipitated with sulfur dioxide which did not reduce significant amounts of polonium. The tellurium which remained after the sulfur dioxide reduction was sufficient to carry the polonium down when the solution was treated with stannous chloride. The reaction was possible only after the complete denitration of the solution because even a small concentration of nitric acid prevented the precipitation of tellurium.

8.3 *Separation of Polonium from Silver.* The siliceous residues contained trace concentrations of silver, gold, platinum, and palladium. These metals precipitated on bismuth in the reduction-with-bismuth step and were also carried down with tellurium in the reduction-with-stannous chloride step. The most troublesome element among the impurities was silver. It was precipitated with tellurium and polonium in the stannous chloride reduction step and remained in solution with polonium when the tellurium was separated by reduction with hydrazine. A quantitative separation from silver was accomplished by the addition of ammonium hydroxide which precipitated the titanium and polonium as hydrated oxides and formed the soluble complex ion, $Ag(NH_3)_2^+$, with silver. A small amount of ammonium chloride was added to prevent the possible formation of silver fulminate. The precipitate of the hydrated oxides of tellurium and polonium did not coagulate, as a rule, until after the addition of a small volume of 30 per cent hydrogen peroxide.

8.4 *Procedure for Separating Polonium from Siliceous Residues.* A total of eight batches of siliceous residues was processed on a pilot-plant scale for the recovery of polonium. Assays of the starting material showed a total polonium content of 40.06 curies. A final yield of 29.31 curies was obtained. The steps in the process are summarized in the following procedure:

1. Extraction with hydrochloric acid.[26] A charge of 42.5 lb of dried residue was placed in a 50-gal glass-lined Pfaudler kettle and treated with 20 gal of 3N hydrochloric acid. The slurry was agitated for 90 min and then allowed to settle for a similar period. Twelve gallons of supernatant liquid was removed, and the residue was treated with another 20 gal of 3N hydrochloric acid. The acid solution was stirred for 20 min; then 10 g of glue (an effective coagulating agent) in dilute aqueous solution was added, and the stirring was continued for 10 min. A

settling period of 30 min gave a clear supernatant liquid of which $19\frac{1}{2}$ gal was removed by siphoning. Filter aid (Dicalite 4200, Johns-Manville) equal to one-half the weight of the dry residue was added and thoroughly mixed with the residue which was then removed by filtration through glass-cloth filters which had been precoated with filter aid. Extraction data are summarized in Table 6.7.

About $4\frac{1}{2}$ gal of the acid solution was recovered in filtering and washing the insoluble material.

Table 6.7—Summary of Data on Extraction

Original charge	42.5 lb (dry)
Original activity	1.0 curie†
Residue after extraction	0.06 curie†
Lead in original residue	9.1 lb
Total volume of acid recovered	36 gal
Activity in filtrate and wash	0.97 curie†
Lead in HCl extract	0.39 lb‡

† Discrepancy due to errors in sampling and counting.

‡ This is close to the solubility of lead sulfate in 3N hydrochloric acid.

The principal impurities in the hydrochloric extract which required attention in subsequent operations were iron, tellurium, selenium, and silver.

2. Denitration with formaldehyde. The clear filtrate was returned to the Pfaudler reaction vessel and heated to approximately 85°C. A 40 per cent solution of formaldehyde was added cautiously in 100- to 200-ml portions until brown fumes ceased to be evolved. After 1200 ml of the formaldehyde solution had been added, the reaction appeared complete, and 300 ml in excess was added. Heating and agitation were continued for at least 30 min after the excess was added.

3. Reduction of iron. Ferric iron must be reduced to the ferrous condition before polonium will deposit on metallic bismuth; consequently fine bismuth powder, finer than 200 mesh, was added until the color of the solution changed from red-brown to green. During the addition of bismuth "fines," dry ice was added to the solution to replace the air in order to prevent the oxidation of iron. When a sample of the solution gave only a faint test for ferric iron with potassium thiocyanate solution, the addition of fine bismuth powder was discontinued. It was found that an excess of fine powder was slow in settling and thus reduced the yield of polonium.

4. First reduction with bismuth. The first concentration of activity was accomplished under carbon dioxide by reduction with 140- to 200-mesh bismuth powder. Approximately 1 kg of bismuth was required to remove the polonium from solution. The relatively large quantity of bismuth was needed because experiments showed that silver, gold, mercury, tellurium, selenium, and traces of other elements were deposited on the bismuth before the polonium was precipitated. Tellurium and selenium which were present in the solution in considerable concentration formed a layer on the surface of the bismuth and thus prevented

the deposition of polonium until after the tellurium and selenium had been completely reduced. The 1000 g of bismuth powder removed more than 95 per cent of the activity from the solution. However, attempts at further concentration of polonium on metallic bismuth were impracticable unless very low concentrations of tellurium and selenium were achieved.

5. Removal of tellurium and selenium. The bismuth powder was dissolved in aqua regia and denitrated with formaldehyde in the usual way. The solution was heated to 90°C, and sulfur dioxide was bubbled through the solution until the precipitation of tellurium appeared complete. The precipitate of tellurium and selenium was removed by filtration and washed with 3N hydrochloric acid. Results confirmed the observation of Guillot and Haissinsky[27] that tellurium and selenium could be precipitated by reduction with sulfur dioxide without carrying down significant amounts of polonium. The filtrate was heated to 85°C and treated with small portions of concentrated nitric acid until the excess sulfur dioxide was completely oxidized as indicated by a change in color of the solution from red-brown to yellow. (The presence of sulfur dioxide interfered with the deposition of polonium in the second reduction with bismuth. Oxidation of the excess sulfur dioxide with nitric acid and subsequent denitration with formaldehyde were steps suggested by C. L. Rollinson. The solution was then heated to 85°C and denitrated by adding formaldehyde.

6. Second reduction with bismuth. The hydrochloric acid solution (about 5N) containing about 90 per cent of the original activity was treated under carbon dioxide with 10 g of 140- to 200-mesh bismuth powder. In $2\frac{1}{2}$ hr 98 per cent of the activity was deposited on the bismuth. Silver and the small amount of tellurium remaining in the solution were also plated on the bismuth. The bismuth was washed three times with 1N hydrochloric acid.

7. Stannous chloride precipitation. The bismuth powder was dissolved in aqua regia and denitrated with formaldehyde. The solution was then cooled to room temperature, and 10 ml of 50 per cent stannous chloride solution was added to reduce tellurium, polonium, and the noble metals to the metallic state. The small amount of tellurium left in solution after the bulk of it was precipitated with sulfur dioxide was usually sufficient to carry the polonium down completely. The precipitate was washed with 4N hydrochloric acid and finally with distilled water.

8. Separation from silver. The precipitate was dissolved in aqua regia and evaporated to dryness. The residue was treated with 300 ml of concentrated ammonium hydroxide containing 10 g of ammonium chloride. The addition of 3 ml of 30 per cent hydrogen peroxide caused the immediate precipitation of tellurium dioxide which carried down 99 per cent of the polonium.

9. Hydrazine precipitation. The tellurium dioxide containing the polonium was dissolved in 200 ml of 6N hydrochloric acid. The solution was treated with 15 ml of 1M hydrazine hydrate and diluted to 300 ml. The hydrochloric acid solution was heated on a water bath for 2 hr and then filtered. The precipitate of tellurium was washed with 4N hydrochloric acid. The filtrate and washings were evaporated to dryness to remove hydrochloric acid. The residue was dissolved in 2.5 ml of concentrated nitric acid and diluted to 25 ml to make a 1.5N solution for electrolysis. A spectrographic analysis indicated the presence of the following impurities: copper, tin, calcium, magnesium, silica, and bismuth.

10. Deposition of polonium by electrolysis. The polonium was deposited on a platinum cathode which was maintained at a potential of 0.0 volt with respect to a normal calomel electrode. The electrolysis of polonium solutions is discussed in Chap. 7.

REFERENCES

1. H. G. Kuivila, H. R. Weimer, and R. G. Yalman, Recovery of Polonium from Radioactive Lead Dioxide, Final Report No. 11, Report MLM-M-1024, July 1, 1945, p. 2.
2. M. Pochon, Trans. Am. Inst. Chem. Engrs., 33: 189-196 (1937).
3. J. H. Lum and W. C. Fernelius, Meeting at Eldorado Mining and Refining Co., Port Hope, Information Report No. 8, Report MLM-M-1490, Dec. 23, 1943.
4. H. R. Weimer, Radiometric Analysis of the Active Lead Dioxide, Final Report No. 1, Report MLM-M-1213, Jan. 20, 1944.
5. H. Freundlich, "Colloid and Capillary Chemistry," H. S. Hatfield, translator, p. 462, E. P. Dutton & Co., Inc., New York, 1922.
6. H. G. Kuivila, H. R. Weimer, and R. G. Yalman, Recovery of Polonium from Radioactive Lead Dioxide, Final Report No. 11, Report MLM-M-1024, July 1, 1945, p. 91.
7. W. Marckwald, Ber., 35: 2287, 4239 (1902).
8. W. C. Fernelius, letter to R. E. Meints, Report MLM-44-11-9, Nov. 1, 1944.
9. W. Marckwald, Ber., 35: 2287 (1902).
10. W. Marckwald, Ber., 35: 2285, 4239 (1902).
11. W. Marckwald, Ber., 36: 2662 (1903).
12. W. Marckwald, Ber., 38: 591 (1905).
13. I. Curie, J. chim. phys., 22: 485 (1925).
14. G. Tammann and W. Reinäcker, Z. anorg. u. allgem. Chem., 156: 276, 280 (1926).
15. T. Bjerge, Z. Physik, 89: 278 (1934).
16. M. Haissinsky, Trans. Electrochem. Soc., 70: 369 (1936).
17. S. H. Styles and C. L. Rollinson, Pilot-plant Silver Process, Final Report No. 39, Report MLM-M-32, Feb. 13, 1947.
18. P. Curie and M. Curie, Compt. rend., 127: 177 (1898).
19. P. Curie and M. Curie, Compt. rend., 127: 175 (1898).
20. P. M. Hamilton and C. L. Rollinson, The Tellurium Process, Final Report No. 36, Report MLM-M-167, June 26, 1947.
21. W. Marckwald, Ber., 35: 4239 (1902).
22. W. Marckwald, Ber., 36: 2663 (1903).
23. M. Curie and A. Debierne, Compt. rend., 150: 387 (1910).
24. M. Haissinsky and M. Guillot, J. phys. radium, 5(7): 422 (1934).
25. A. Karl, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa, 140: 201 (1931).
26. H. G. Kuivila, H. R. Weimer, and R. G. Yalman, Recovery of Polonium from Radioactive Lead Dioxide, Final Report No. 11, Report MLM-M-1024, July 1, 1945, p. 88.
27. M. Guillot and M. Haissinsky, Bull. soc. chim., 2(5): 240 (1935).

Chapter 7

POLONIUM FROM IRRADIATED BISMUTH: CHEMICAL SEPARATION

By Lloyd B. Gnagey, James M. Goode, G. D. Nelson,
and J. W. Wright

1. INTRODUCTION

Naturally occurring sources of polonium, such as the lead-containing wastes from uranium, vanadium, and radium refining operations (Chaps. 1 and 6) were first used at the Dayton Project as the raw material from which polonium was purified from the preparation of neutron and alpha sources. However, an investigation[1,2] of available sources of naturally occurring polonium-bearing ores indicated that (1) polonium could not be recovered from these sources without processing prohibitively large quantities of raw material; (2) in commercial refining methods polonium was not concentrated in any particular step of the process, but it could be found in several of the solutions or residues, making processing of more than one waste fraction necessary; and (3) the supply of refinery residues available for processing was uncertain and depended upon operating schedules of industries primarily concerned with the production of uranium and radium.

The conversion of Bi^{209} to Bi^{210} (RaE) had been reported,[3] and, because this isotope decays rather rapidly to Po^{210} (RaF), bismuth which had been subjected to neutron bombardment appeared to be a more suitable source of polonium than naturally occurring ores. Relatively pure bismuth was available in commercial quantities, and separation of polonium from a raw material containing impurities of the order of a few parts per million would be less difficult than from refinery wastes containing larger amounts of impurities. Methods for irradiating bismuth by neutron bombardment and for separating polonium from irradiated bismuth were developed, and substantially all polonium purified at the Dayton Project and Mound Laboratory was prepared by these methods.

2. IRRADIATION OF BISMUTH

2.1 *General.* Transmutation of an element was first observed by Rutherford[4] in 1919 when he bombarded several light elements with alpha particles. Subsequent experiments showed that he had succeeded in transmuting nitrogen to oxygen by an (α,p) process. Continued experiments by Rutherford and Chadwick[5] showed that many of the light elements were susceptible to transmutation by alpha-particle bombardment; sufficient energy was not available to penetrate the coulombic barrier of the heavier nuclei.

The development of the cyclotron in 1931 by Lawrence and his associates[6] provided a method for accelerating particles with sufficient penetrating power to attack the nucleus of the heavier elements. Livingood,[7] working with the cyclotron, showed that polonium could be produced (from Bi^{210} decay) by bombarding Bi^{209} with deuterons. Amaldi and his associates[3] had previously shown that polonium could be produced in a similar manner by bombarding Bi^{209} with neutrons. The quantities of Bi^{210} and polonium produced by either neutron or deuteron bombardment of Bi^{209} were minute and detectable only by sensitive radiation-detection instruments. The successful operation of a nuclear reactor in 1942 provided intense neutron sources for the first time and thus made possible the formation of weighable quantities of polonium.

2.2 *Polonium by Deuteron Bombardment.* The first artificial production of polonium by deuteron bombardment was accomplished in 1936 by Livingood.[7] He reported the effects of bombardment of copper, zinc, antimony, ruthenium, and bismuth with high-energy deuterons. The bismuth-deuteron reaction

$$_{83}Bi^{209} + {}_1H^2 \rightarrow {}_{83}Bi^{210} + {}_1H^1$$

is of particular interest because Bi^{210} decays to Po^{210} by the emission of a beta particle. Bismuth was bombarded with 5.4-Mev deuterons for a total of 13 μa-hr. After this activation Livingood was able to follow the beta decay of Bi^{210} (RaE) as well as the growth of alpha-active Po^{210} (RaF). As various high-energy particle accelerators were built, much work was done in the field of artificial production of radioisotopes.

2.3 *Transmutation by Neutrons.* In 1934 and 1935 Amaldi and coworkers[3] bombarded 59 elements with neutrons. They used a radium-beryllium neutron source which had a neutron intensity of 8×10^5 neutrons/sec, and they found conclusive evidence of transmutation of the light elements and somewhat less evidence of transmutation of the heavy elements. They reported that a shield of water or paraffin around the target greatly increased the effectiveness of the neutrons, and they attributed this effect to slowing down, or "moderating," of the neutrons by collision with the hydrogen atoms in the shield.

Bi^{209} was one of the heavy elements for which successful transmutation was reported. This element was converted to Bi^{210} (RaE) by neutron absorption according to the equation

$$_{83}Bi^{209} + {}_0n^1 \rightarrow {}_{83}Bi^{210} + \gamma \qquad (7.1)$$

2.4 *Production of Polonium.* The artificial production of Bi^{210} occurs by an (n,γ) nuclear reaction. The neutron is absorbed by the bismuth nucleus, and any excess energy is released through the emission of a photon as shown by Eq. 7.1. The Bi^{210} decays with a 5-day half life to Po^{210} by the emission of a beta particle:

$$_{83}Bi^{210} \rightarrow {}_{84}Po^{210} + \beta^-$$

Po^{210}, with a 138.4-day half life, decays to stable Pb^{206} by the emission of an alpha particle:

$$_{84}Po^{210} \rightarrow {}_{82}Pb^{206} + \alpha$$

These processes occur simultaneously as bismuth is irradiated with neutrons and are the fundamental reactions that govern the rate of formation of polonium in a nuclear reactor.

Bi^{210} and Po^{210} absorb neutrons during irradiation in a reactor; however, the activation cross sections of these substances, although not known with precision, are so small that no appreciable quantities of these materials are lost during irradiation. Consequently no correction for this loss is made in calculations of polonium yield.

An isomer of Bi^{210}, formed during neutron bombardment of Bi^{209}, has been reported.[8,9] This isomer decays by alpha emission to Tl^{206}, which decays by beta emission to Pb^{206}. The half life of this isomer is reported[9] as 1×10^6 years, and, because of this slow rate of decay, this isomer remains with the bismuth fraction after separation of polonium.

2.5 *Polonium Yield.* The yield of polonium from bismuth irradiated in a reactor may be calculated from consideration of the production of Bi^{210}, the decay of Bi^{210} to Po^{210}, and the decay of Po^{210} to Pb^{206}. For this calculation the following symbols may be used:

F = average reactor flux, number of neutrons per square centimeter per second
σ = neutron activation cross section, Bi^{209} to Bi^{210}, 10^{-24} cm^2
d = density of Bi^{209}, grams per cubic centimeter
w = atomic weight of Bi^{209}, grams per mole
A = Avogadro's number, atoms per mole
t = time, days
B = rate of growth of Bi^{210} with no decay, atoms per cubic centimeter per day
λ_1 = decay constant of Bi^{210}, days^{-1}

λ_2 = decay constant of Po^{210}, $days^{-1}$
N_1 = number of Bi^{210} atoms per cubic centimeter at time t
N_2 = number of Po^{210} atoms per cubic centimeter at time t
c = curies of polonium produced in time t per kilogram of bismuth
κ = a factor which corrects for the difference in time units and is 24 × 60 × 6, or 86,400

Bi^{210} is formed in the reactor at a rate B given by

$$B = \frac{F\sigma d}{w} \kappa A \tag{7.2}$$

Bi^{210} decays to Po^{210} with a decay constant λ_1. If N_1 is the number of Bi^{210} atoms per cubic centimeter at time t, then the equation for the rate of growth of Bi^{210} is

$$\frac{dN_1}{dt} = B - \lambda_1 N_1 \tag{7.3}$$

At time t = 0, $N_1 = 0$; hence the solution to Eq. 7.3 is

$$N_1 = \frac{B}{\lambda_1} (1 - e^{-\lambda_1 t}) \tag{7.4}$$

Also, at time t, while the atoms of Bi^{210} are decaying at a rate $\lambda_1 N_1$, the Po^{210} atoms are in turn decaying to Pb^{206} at a rate $\lambda_2 N_2$. The equation for the growth of Po^{210} is therefore

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \tag{7.5}$$

If the value of N_1 in Eq. 7.4 is substituted in Eq. 7.5, the rate of growth of Po^{210} is shown to be

$$\frac{dN_2}{dt} = B(1 - e^{-\lambda_1 t}) - \lambda_2 N_2 \tag{7.6}$$

At time t = 0, $N_2 = 0$; therefore the solution to Eq. 7.6 is

$$N_2 = B\left[\frac{1}{\lambda_2} + \frac{e^{-\lambda_1 t}}{\lambda_1 - \lambda_2} - \frac{\lambda_1 e^{-\lambda_2 t}}{\lambda_2(\lambda_1 - \lambda_2)}\right] \tag{7.7}$$

This is the general equation for the growth of polonium in neutron-irradiated bismuth.

Equation 7.7 may be converted to a more useful form, in terms of curies of polonium per kilogram of bismuth, by the factor

$$c = \frac{\lambda_2 N_2 \times 10^3}{d(3.7 \times 10^{10})} = \frac{\lambda_2 N_2}{d(3.7 \times 10^7)} \tag{7.8}$$

Substituting the value for N_2 from Eq. 7.7 in Eq. 7.8 gives another general equation for the growth of polonium in neutron-irradiated bismuth.

$$c = \frac{F\sigma A}{w(3.7 \times 10^7)} \left(1 + \frac{\lambda_2 e^{-\lambda_1 t}}{\lambda_1 - \lambda_2} - \frac{\lambda_1 e^{-\lambda_2 t}}{\lambda_1 - \lambda_2}\right) \tag{7.9}$$

The growth of polonium in neutron-irradiated bismuth is shown in Fig. 7.1.

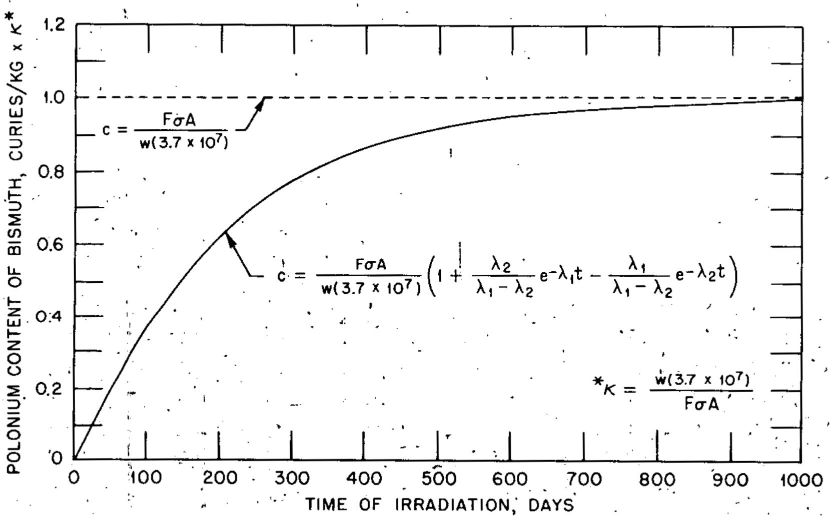


Fig. 7.1—Growth of polonium in neutron-irradiated bismuth.

Equation 7.9 shows that with prolonged irradiation the polonium produced per kilogram of bismuth will reach a saturation value, at which time the rate of growth of polonium is equal to the rate of decay of the polonium. This saturation value will be reached as t approaches infinity.

$$\lim_{t \to \infty} (c) = \frac{B}{d(3.7 \times 10^7)} = \frac{F\sigma A}{w(3.7 \times 10^7)} \tag{7.10}$$

The manner in which this limit is approached is shown by the growth curve, Fig. 7.1.

2.6 *Maximum Rate of Growth of Polonium.* The rate of growth of polonium in bismuth subjected to neutron irradiation may be obtained from the derivative of Eq. 7.9,

$$\frac{dc}{dt} = \frac{F\sigma A\lambda_1\lambda_2}{w(3.7 \times 10^7)(\lambda_1 - \lambda_2)} \left(e^{-\lambda_2 t} - e^{-\lambda_1 t}\right) \tag{7.11}$$

From Eq. 7.11 it can be seen that, at time $t = 0$ and at time $t = \infty$, the rate of growth of polonium is zero. The rate of growth of the polonium will, then, have a maximum, and consequently

$$\frac{d^2c}{dt^2} = \frac{F\sigma A\lambda_1\lambda_2}{w(3.7 \times 10^7)(\lambda_1 - \lambda_2)} \left(\lambda_1 e^{-\lambda_1 t^*} - \lambda_2 e^{-\lambda_2 t^*}\right) = 0 \tag{7.12}$$

The time of maximum rate of growth t^* is determined from Eq. 7.12:

$$t^* = \frac{1}{\lambda_1 - \lambda_2} \ln \frac{\lambda_1}{\lambda_2} = 24.81 \text{ days} \tag{7.13}$$

The numerical value of Eq. 7.13 is based on values for the half lives of Bi^{210} and Po^{210} of 4.989 and 138.401 days, respectively. The rate of growth of polonium in neutron-irradiated bismuth is shown in Fig. 7.2.

2.7 *Growth of Polonium After Irradiation Ceases.* The Bi^{210} content of the irradiated bismuth at the time of removal from the reactor causes the polonium content to increase after removal of the irradiating flux. The polonium content will reach a maximum at a time t''_m after removal of the bismuth from the reactor, which depends upon the half lives of Po^{210} and Bi^{210} and the time of irradiation. The number of polonium atoms N''_2 present in the bismuth at a time t'' after an irradiation time t' may be found.

Let N_2^* be the number of polonium atoms present in the Bi^{209} at the end of an irradiation time t'.

From Eq. 7.7

$$N_2^* = \frac{B}{\lambda_2}\left(1 + \frac{\lambda_2 e^{-\lambda_1 t'}}{\lambda_1 - \lambda_2} - \frac{\lambda_1 e^{-\lambda_2 t'}}{\lambda_1 - \lambda_2}\right)$$

Let N_1^* be the number of Bi^{210} atoms present in the Bi^{209} at the end of irradiation time t'. From Eq. 7.4

$$N_1^* = \frac{B}{\lambda_1}\left(1 - e^{-\lambda_1 t'}\right)$$

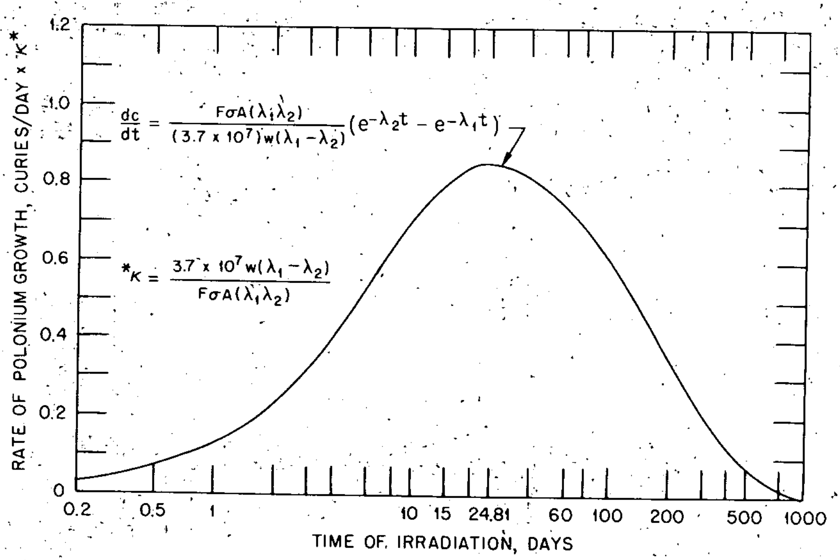


Fig. 7.2—Rate of growth of polonium in neutron-irradiated bismuth.

Let N_1'' be the number of Bi^{210} atoms present in the Bi^{209} at a time t'' after an irradiation time t'. N_1'' may be obtained from the differential equation

$$\frac{dN_1''}{dt''} = -\lambda_1 N_1''$$

and from the condition that $N_1'' = N_1^*$ when $t'' = 0$. From

$$N_1'' = N_1^* e^{-\lambda_1 t''}$$

N_2'', the number of polonium atoms present in the Bi^{209} at any time t'' after an irradiation time t', may then be found from the differential equation

$$\frac{dN_2''}{dt''} = \lambda_1 N_1'' - \lambda_2 N_2'' = \lambda_1 N^* e^{-\lambda_1 t''} - \lambda_2 N_2'' \qquad (7.14)$$

This equation may be solved by assuming a solution of the form

$$N_2'' = A_0 + A_1 e^{-\lambda_1 t''} + A_2 e^{-\lambda_2 t''}$$

where A_0, A_1, and A_2 are constants, and from the condition that $N_2'' = N_2^*$ at a time $t'' = 0$. The solution is

$$N_2'' = \frac{B}{\lambda_2(\lambda_1 - \lambda_2)}\left[\lambda_1 e^{-\lambda_2 t''} - \lambda_2 e^{-\lambda_1 t''} + \lambda_2 e^{-\lambda_1(t'+t'')} - \lambda_1 e^{-\lambda_2(t'+t'')}\right] \qquad (7.15)$$

The time t''_m for maximum Po^{210} content of the Bi^{209} after a period of irradiation of time t' may be obtained by differentiating Eq. 7.15, setting the resulting equation equal to zero, and solving for t''_m. That time is given by

$$t''_m = \frac{1}{\lambda_1 - \lambda_2} \ln \frac{1 - e^{-\lambda_1 t''}}{1 - e^{-\lambda_2 t'}} \qquad (7.16)$$

This time is shown in Fig. 7.3 as a function of the time of irradiation.

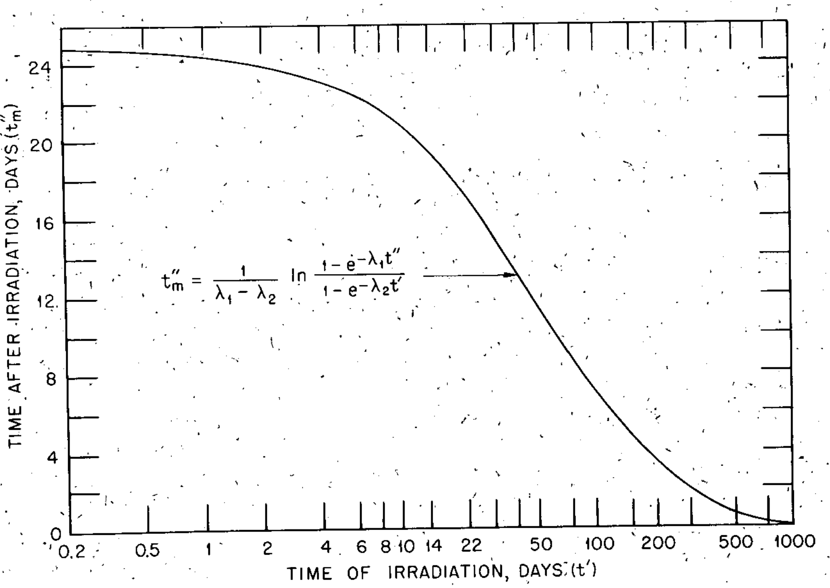


Fig. 7.3—Maximum polonium content as a function of irradiation time t'.

2.8 *Factors Controlling Formation of Polonium.* (a) *General.* The factors which control the formation of polonium by bismuth irradiation are indicated in Eq. 7.9. From this equation it can be seen that the formation of polonium, in terms of curies of polonium per kilogram of bismuth, is dependent on the decay constants of Po^{210} and Bi^{210} (λ_1 and λ_2), on the irradiating neutron flux (F), on the neutron-activation cross section of Bi^{209} (σ), and on the time of irradiation (t).

(b) *Half Life.* The decay constant λ of a radioactive material is related to the half life $T_{1/2}$ of that material by the relation

$$\lambda = \frac{\ln 2}{T_{1/2}} \cong \frac{0.693}{T_{1/2}}$$

The half lives of Bi^{210} and Po^{210} were known approximately because of their occurrence as natural decay products of radium. Values of 5 and 140 days for the half lives of Bi^{210} and Po^{210}, respectively, were used for purposes of computation, and recent determinations of these half lives have not appreciably changed these values.

Lockett and Thomas[10] report a value of 4.989 ± 0.013 days for the half life of Bi^{210}. This value was obtained, with a beta-sensitive electroscope, by counting the beta particles from a sample of Bi^{210} of 99.99 per cent purity. The time required for the deflected electroscope to return to zero was measured at intervals over a period of 7 to 33 days (7 days allowed the short-half-life impurities to decay). The electroscope was standardized with a radium sample before and after each measurement.

Eichelberger and coworkers[11] report a value of 138.4005 ± 0.0051 days for the half life of Po^{210}. This value was obtained by measuring the heat produced by the radioactive decay of polonium. The heat of five polonium samples (greater than 95 per cent purity) was measured in four steady-state resistance-bridge calorimeters (Chap. 2, Sec. 2.3). Observations of the heat evolved from the five samples were made over periods of time ranging from 105 to 617 days. The calorimeters used in this determination are described in Chap. 10.

(c) *Bi^{209} Cross Section.* The formation of polonium is a function of the neutron-activation cross section of Bi^{209}. The earliest workers in the field of neutron irradiation of bismuth could not measure the neutron-activation cross section, but they did observe that it was very small. Goldhaber and O'Neal[12] reported the neutron-activation cross section of Bi^{209} as less than 0.1 barn (0.1×10^{-24} sq cm). Later work by Colmer and Littler[13] gave a value of 0.0205 ± 0.0015 barn for the activation cross section of Bi^{209} for thermal neutrons. Eggler and Hughes[14] reported 0.016 ± 0.003 barn as the activation cross section of Bi^{209} for thermal neutrons.

The value of the cross section reported by Colmer and Littler and the value reported by Eggler and Hughes were both obtained by irradiating a sample of Bi^{209} with the thermal-neutron flux of a reactor.

The flux was measured by irradiating, along with the sample of bismuth, a sample (usually indium foil) whose activation cross section was accurately known. From the size, shape, time of irradiation, and induced activity of the indium-foil standard, the reactor neutron flux was determined and the activation cross section of Bi^{209} was calculated from the determined thermal flux of the reactor.

A less direct method of determining isotope neutron cross sections is by the "pile-oscillation" method, which gives a larger value for the cross section of Bi^{209} than that reported above. The neutron-absorption cross section is determined by moving a given sample in and out of the reactor and observing the oscillation of the operational level of the reactor. This fluctuation is compared to that produced by a standard for which the cross section is known. By this method, Harris and coworkers[15] obtained a value of 0.039 barn for the absorption cross section of Bi^{209}. Another value, obtained by the same method, is in fair agreement with the Harris value. Eggler and Hughes[14] report a value of 0.033 barn for the neutron-absorption cross section of Bi^{209}.

The difference between the Bi^{209} neutron cross section obtained by the pile-oscillation method and by the activation method may be explained by a recent report by Neuman and coworkers.[8] They found that a constant alpha activity remained in the Bi^{210} fraction after the lead and polonium had been separated from the irradiated Bi^{209} and after the Bi^{210} residue had been allowed to decay for 6 months. This indicated the production of an isomeric state of Bi^{210} during irradiation.

A more recent report by Levy[9] has confirmed this theory. He used previously purified irradiated bismuth concentrated by magnetic separation, and he found a long-lived alpha activity associated with the mass-210 fraction. Since the RaE had been allowed to decay and the polonium was removed from the bismuth before the magnetic separation, the observed alpha activity could have originated only from a Bi^{210} isomer. Further studies established the energy of this alpha particle to be 4.935 ± 0.020 Mev. Palevsky, Hughes, and Eggler[16] suggested an approximate value of 10^6 years for the half life of this isomer, and this value is based on the half life of Po^{210} and their measured values for the absorption and polonium-activation cross sections of Bi^{209}.

(d) *Neutron Flux.* The formation of polonium by neutron irradiation of Bi^{209} is also a direct function of the available neutron flux. The neutron flux (from radium or radon and beryllium mixtures) available to the early nuclear energy investigators was quite small compared to that produced in a nuclear reactor. Fermi and coworkers[17] report using a neutron source of 8.5×10^5 neutrons/sec. If all these neutrons could have been moderated and utilized through an area of 1 sq cm, approximately 10^{-7} curie of polonium per kilogram of bismuth would have been formed after 25 days of irradiation.

By comparison, the Clinton reactor[18] at Oak Ridge, Tenn., attained a flux of 1.3×10^{11} neutrons/sq cm/sec within a short time after being placed in operation. A concentration of approximately 0.014 curie of polonium per kilogram of bismuth results from a flux of this magnitude after a 25-day irradiation period. The irradiation of bismuth in a reactor having a greater flux than that of the Clinton reactor would increase the concentration of polonium in the bismuth by a factor which is proportional to the ratio of neutron fluxes used (assuming the same irradiation time for both cases).

(e) *Length of Time of Irradiation.* The formation of polonium in a reactor is a function of the length of time of bismuth irradiation. For polonium formation a much more important factor is the product of flux and time, i.e., the same concentration of polonium in bismuth may be obtained in a short time with a high flux or a longer time with a lower flux. However, saturation limits the length of time that it is economical to irradiate bismuth. Saturation occurs when the amount of polonium formed in the bismuth equals the amount of polonium which decays.

For the synthesis of polonium for the preparation of neutron sources and alpha sources, bismuth was irradiated for a sufficient time for the polonium concentration in the bismuth to reach approximately 50 per cent of the saturation value. If a greater exposure time had been used, the increase in polonium concentration would not have corresponded to the increase in exposure time because of the exponential nature of the growth curve, Fig. 7.1. If a shorter time had been used, the concentration of polonium in bismuth would have been less, which would have necessitated the processing of larger amounts of bismuth for a given polonium yield.

2.9 *Raw Material.* (a) *Bismuth Purity.* A high purity of bismuth to be irradiated for the formation of polonium is necessary in order to prevent the formation of undesirable isotopes which might cause difficulty in subsequent processing operations. The original specifications for bismuth, set in 1943, are given in Table 7.1.

The Metallurgical Laboratory at Chicago analyzed[20] the first batch of bismuth received, and the results of their investigation are shown in Table 7.2.

It was assumed[21] that these impurities would cause no appreciable difficulty due to their activation by slow neutrons; however, little was known about the silver isotope having a 270-day half life. Only after actual irradiation of Bi^{209} in a reactor was it learned that silver would cause trouble in processing.

Ag^{109} is transformed into Ag^{110} by an (n,γ) reaction. Ag^{110} is a beta and gamma emitter with a half life of 270 days, and it has an isomer with a much shorter half life. The long-lived isomer proved troublesome by increasing the radiation hazard of the slugs. The silver content of the bismuth for irradiation was reduced to as low as 0.03 ppm; however, current specifications require only that the silver content be less than 0.1 ppm.

Table 7.1—Specifications for Bismuth To Be Irradiated in a Reactor[19]

Constituent	Initial values	Later values
Bi (assay)	99.9+%	99.9+%
As	<10 ppm	<0.10 ppm
Fe	<1000 ppm	<10 ppm
Pb	<1000 ppm	<1000 ppm
Sb	<10 ppm	<0.10 ppm

Table 7.2—Results of Spectroscopic Analysis of Bismuth

Constituent	Amount present	Constituent	Amount present
Ag	4 ppm	Hg	Absent
As	<2 ppm	In	Absent
Au	Absent	Mg	<10 ppm
B	<1 ppm	Mn	Absent
Be	Absent	Mo	Absent
Bi	Large amount	Ni	Absent
Ca	100 ppm	P	Absent
Cd	<0.2 ppm	Pb	<1 ppm
Co	Absent	Pd	Absent
Cr	Absent	Sb	5 ± 3 ppm
Cu	<10 ppm	Si	Absent
Fe	<5 ppm	Sn	Absent
Ge	Absent	Ta	Absent

(b) *Preparation of Bismuth for Irradiation.* Bismuth for irradiation purposes was used in two general forms, bricks and slugs. The bismuth bricks which were irradiated in the Clinton reactor were 12 by $3\frac{3}{4}$ by $3\frac{3}{4}$ in. in size, and each weighed approximately 58 lb. The bricks were placed in experimental "holes" in the reactor.

Bismuth bricks were also used for gamma-ray shielding around the Clinton reactor. These bricks were exposed for long periods of time, but the neutron flux was of such a low value that the polonium content in the bricks was small. Although they were considered as a possible source of polonium, they were never used because of the volume of material to be processed.[22]

The slugs were cylindrical rods of bismuth approximately 1½ in. in diameter (although other slug diameters were used) and were used in two different lengths.

(c) *Bismuth Canning.* The first bismuth to be irradiated in the Clinton reactor was in the form of bare slugs. The use of unprotected bismuth for irradiation purposes proved to be undesirable. When the first irradiated slugs were discharged from the reactor, one slug was broken and chips fell into containers of uranium slugs from which the bismuth chips had to be separated by hand at considerable hazard to personnel. It was feared that movement of the bismuth slugs in and out of the reactor, with the associated mechanical wear and chipping, would lead to an accumulation of foreign matter within the reactor and necessitate frequent decontamination of the reactor. To reduce the danger of contamination of the reactor and surroundings during irradiation and subsequent handling of irradiated material, a protective aluminum jacket, or can, was provided for the bismuth.[23]

The bismuth slugs were cast slightly oversize and machined to fit closely into aluminum jackets. After the bismuth slug was inserted into this aluminum can, an aluminum plate was placed over the exposed end of the bismuth slug and the plate was welded to the can with a heliarc welder. Some slugs are jacketed with tubing to which suitable ends are applied and are securely welded to the tubing.

The aluminum used for the can is 2-S aluminum, which may contain the following impurities: iron, manganese, copper, lead, tin, zinc, silicon, titanium, nickel, magnesium, chromium, vanadium, bismuth, and gallium. From the standpoint of radiation hazard, iron is of significance, producing, upon exposure to neutron irradiation, a gamma-active isotope which has a half life of 45 days. The other impurities are of little importance because the half lives of the radioactive materials produced are so short that these materials decay to safe values in the slug cooling-off period. An exploded view of a 4-in. slug and can assembly is shown in Fig. 7.4.

3. HANDLING AND STORAGE OF IRRADIATED BISMUTH

3.1 *General.* The storage and handling of irradiated bismuth is not difficult when the concentration of polonium is less than 0.1 ppm. As the polonium concentration is increased, the beta and gamma radiation from the irradiated slug becomes appreciable and constitutes a health hazard to operating personnel.[24]

3.2 *Shipment.* The shipment of irradiated bismuth can be made by truck, air transport, or railroad car. The radiation intensity at the surfaces of packages of radioactive materials and the amount of contamination on these packages must not exceed limits established for shipment of radioactive substances.[25]

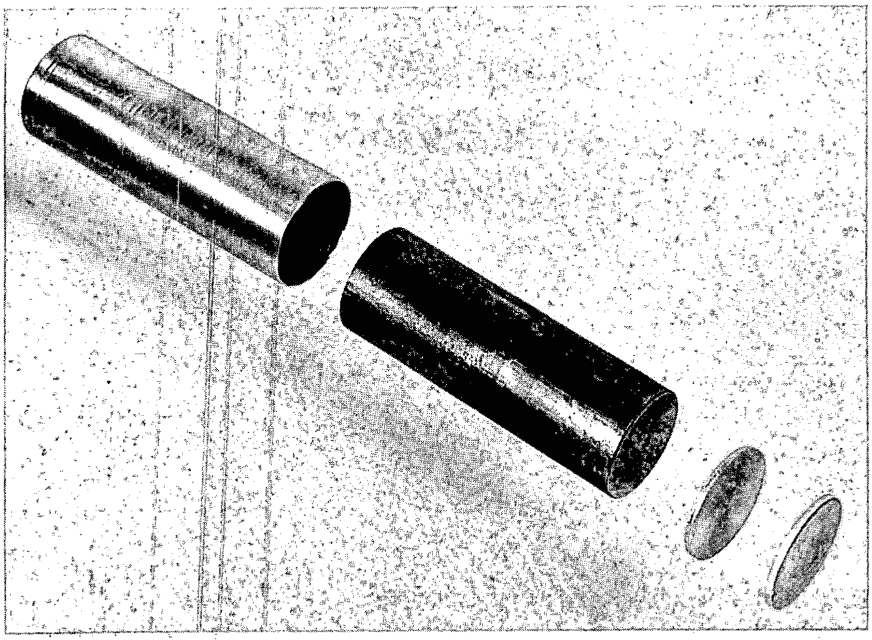


Fig. 7.4 — Exploded view of a 4-in. slug and can assembly.

Bismuth bricks irradiated in the Clinton reactor were shipped in individual wooden boxes which were constructed to closely fit each brick. The concentration of polonium in each brick and the number of bricks in each shipment were such that no difficulty was experienced in transporting them.

Irradiated bismuth slugs may be transported in containers, or casks, which are cylindrical in shape and which are fitted with a nest of tubes, each tube being large enough to loosely hold one slug. The space between the tubes may be filled with lead to absorb gamma radiation from the slugs. These casks should be securely fastened in a second box such that radiation measured at any surface of the box is within the permissible limits specified by shipping regulations.

3.3 *Storage.* Bismuth bricks which had been irradiated in the Clinton reactor were received at the Dayton Project and were stored temporarily in a small tile-lined cavity in the floor near the area where they were to be processed. When irradiated bismuth slugs became available to the Dayton Project, this method of storage was inadequate. A method of storage for irradiated bismuth slugs was developed[26] which would provide health protection for personnel.

A steel safe, or storage cabinet, was built which was provided with doors on the front and back sides. Tubes of somewhat shorter length than the depth of the safe were positioned horizontally in the storage cabinet, and the space between the tubes and the inner cabinet wall was filled with lead. The tubes were large enough to receive slugs loosely, and the doors of the cabinet afforded access to the tube ends. Consequently slugs were easily inserted or removed from either side of the cabinet. Each tube was provided with a removable lead plug which reduced radiation effects from the stored slugs.

Another storage method was developed wherein irradiated slugs were stored under water, and as a result radiation from the slugs was reduced to a value which would offer no hazard to personnel. A tile-lined storage pool was constructed, and an inclined storage rack was installed in the pool. This rack was provided with holes into which slugs could be inserted or removed by tongs. A periscope was installed in the pool; therefore any slug could be inspected and its identification markings could be examined without lifting the slug above the surface of the water.

4. ASSAY OF IRRADIATED BISMUTH SLUGS

4.1 *General.* The quantity of polonium in irradiated bismuth may be calculated by the methods described in Sec. 2, but such calculations are time-consuming, and complete data for making the computations frequently are lacking. A direct method for determining the quantity of polonium in each piece of irradiated bismuth is desirable for computing material balances.

4.2 *Chemical Assay.* The quantity of polonium in irradiated bismuth slugs (or bricks) may be determined by taking a representative sample from each slug, dissolving a known weight of this sample in suitable reagents, diluting the solution to a definite volume, and mounting a small aliquot on a suitable slide.[27] This slide is counted in an alpha counter, and the quantity of polonium contained in the slugs is then calculated from the observed counting rate, dilution factor of the solution, and the weight of the sample used.

4.3 *Gamma Assay.* A method of slug assay which does not require the taking of samples of the piece to be assayed is desirable in order to reduce the contamination of equipment and the hazards to personnel. Gamma radiation[28-31] emitted by slugs or bricks of irradiated bismuth has been used as a means of estimating polonium content. Certain impurities in the bismuth, or in its jacket (for example, silver), are rendered gamma active by irradiation in a reactor. For any particular lot of bismuth and jacket material, the quantity of impurities may be assumed to be equally distributed in all pieces fabricated from this lot; consequently gamma radiation due to these substances can be considered to be a constant fraction of the total radiation emitted by the slug. The total gamma radiation from an irradiated bismuth slug is caused by impurities in the bismuth and by polonium, and, because the radiation caused by the impurities is a constant fraction of the total, the total radiation is a function of the polonium content. Thus, in slugs fabricated from a particular lot of bismuth, the polonium content of each slug may be estimated from a measurement of the total gamma radiation from each slug.

Gamma radiation may be measured by means of a Lauritsen electroscope, as shown in Fig. 7.5. The electroscope is mounted upon a stand which is provided with one or more V-shaped receptacles adapted to receive a slug in order that all slugs are measured at a fixed distance from the electroscope. With a slug positioned in the stand, the electroscope is charged by an electrical device so that the indicating fiber of the electroscope is positioned at a predetermined mark on the scale. The time required for the fiber to traverse a definite number of scale divisions is recorded, and the reciprocal of this value is computed. This reciprocal of the discharge time of the electroscope is used as a measure of the gamma radiation from the slug.

Any extraneous ionizing radiation passing through the electroscope will cause the indicating fiber to move over the scale in a manner similar to radiation from a slug. This extraneous radiation must be measured at frequent intervals by observing the discharge time of the electroscope without any slug in position, computing the reciprocal of the discharge time, and deducting this value from the reciprocals of the discharge times of all slugs measured during the time interval.

An error caused by decay of polonium and active impurities may be introduced unless all slugs from one lot are measured within a comparatively short time interval (of the order of several hours). A correction for this error may be made by selecting several slugs from one lot as "standards" and measuring the activity from these slugs frequently. By determining the time rate-of-change of the standard slugs, the radioactivity measurements of all slugs can be corrected to values which they had at any selected time since they were removed from the reactor.

The reciprocals determined as described are relative values; that is, the radioactivity content of one slug is referred to the others in the same lot. If the polonium content of one or more of these slugs is known, the polonium content of the others may be calculated from the corresponding relative values. Several slugs from each lot may be taken for analysis (Sec. 4.2) and the polonium content determined. These data are plotted on coordinate cross-section paper, and the relation of relative value to polonium content is calculated. From this the quantity of polonium in any slug in the lot can be computed.

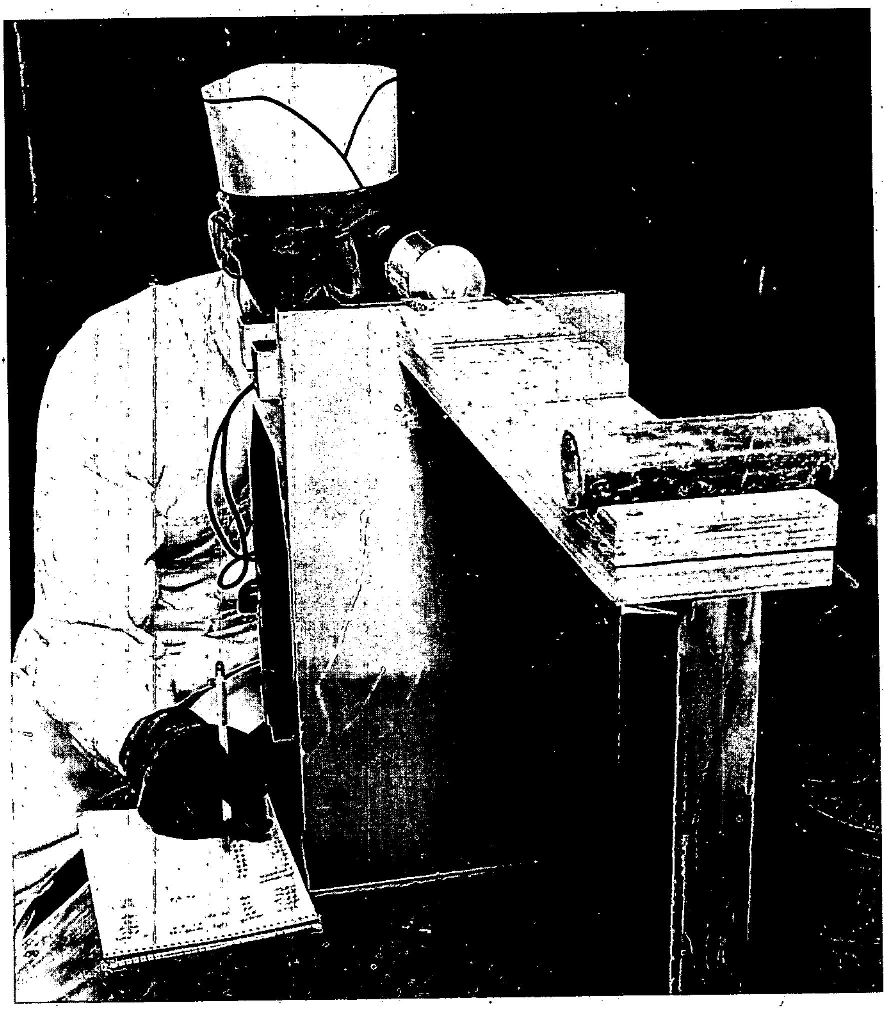


Fig. 7.5—Measurement of gamma radiation from slug.

Gamma radiation from slugs may be measured by means of an electrometer such as that described in Chap. 9, Sec. 3.7. This instrument is adapted to installation in a storage pool of water and is constructed in such a manner that measurements may be made on slugs without removing them from the pool. Relative values of individual slugs are indicated on an arbitrarily numbered scale, the values of which may be used to calculate the polonium content of the slug as described in the previous paragraph.

4.4 *Calorimetric Assay.* The quantity of polonium in a slug may be determined by measuring the quantity of heat generated by the decay of the radioactive material in the slug. During a period of approximately 30 days after the discharge of slugs from the reactor, substantially all of the Bi^{210} will have decayed to Po^{210}; consequently the calorimetric measurements made after this "cooling-off" period will primarily record the heat generated by the decay of polonium. The polonium content of each slug can be computed from calorimetric measurements obtained as described in Chap. 10.

4.5 *Calculated Values.* The quantity of polonium in individual slugs may be calculated from equations developed in Sec. 2 if the reactor neutron flux around that slug is known. If the distribution of neutron flux along the axis of the slugs in a reactor is known and the polonium content of any one slug in the lot has been determined, the polonium content of all other slugs in the lot may be calculated since, as was indicated in Sec. 2, the polonium formed in a slug is proportional to the neutron-flux intensity. A method[32,33] for calculating the amount of Po^{210} in irradiated bismuth slugs was developed which was based on the assumption that the reactor-flux intensity was a cosine function along the axis of the reactor.

5. DECANNING IRRADIATED BISMUTH SLUGS

5.1 *General.* Where subsequent processing operations are such that substances in the aluminum jacket do not interfere, the jacket may be dissolved with the bismuth; however, removal of the jacket before dissolution of the slugs is generally preferred. This may be accomplished by several different methods, but due consideration must be given to the radiation hazards involved.

Alloying elements in the jacket material[36] become radioactive as a result of neutron irradiation in a reactor; in particular, iron, which forms an isotope having a 45-day half life, is a radioactive contaminant which must be considered. Traces of cobalt and zinc may be present in the jacket, and these form isotopes having half lives of 5.3 years and

250 days, respectively. These radioactive elements emit gamma radiation which may be of sufficient intensity to cause a serious hazard to personnel. The decanning operation is therefore performed in a suitably shielded enclosure.

5.2 *Mechanical Decanning.* The bismuth bricks irradiated in the Clinton reactor were enclosed in a thin aluminum can which was fabricated in such a manner that the open end could be crimped shut after the brick had been inserted. Unfastening the crimped end of this can permitted the irradiated brick to be withdrawn.

Bismuth slugs may be decanned[34] by use of a mechanical apparatus such as that shown in Fig. 7.6. In the operation of this equipment, a slug is placed on the lower rollers and the upper roller is forced into contact with the slug at a predetermined pressure. The lower rollers are rotated by an electrically driven motor at a constant roller-surface velocity. After approximately 15 sec of rolling, the slug jacket is loosened and the end caps are separated from the jacket shell; hence the slug may be removed from the jacket. Figure 7.7 shows a slug which has been decanned by this procedure.

The rolling operation makes a clean fracture of the joint at which the end caps are attached to the jacket shell and stretches the jacket shell so that the slug may be removed easily. Heavy pressure and long rolling times result in work-hardening of the jacket and excessive flaking of the bismuth slug; insufficient pressure and short rolling times do not cause complete loosening of the jacket.

An appreciable amount of heat is generated in slugs during irradiation in a reactor, and, to obtain efficient cooling of the slug, heat must be readily transferred from the slug to the jacket. This requires a tight fit of slug and jacket in order that a large metal-to-metal contact area is attained. Removal of the jacket by means of hydraulic or pneumatic pressure applied to one end of the slug, after removal of both end caps, is not practical because friction caused by the tight fit of slug and jacket is such that excessive pressures are required to cause relative movement of slug and jacket. These pressures result in crushing and breaking of the slug and rupture of the jacket. The close fit at the ends of the slug makes cutting of the end cap a critical operation because the slug must be accurately positioned in order to properly locate the cutting mechanism.

5.3 *Decanning by External Heat.* A number of bricks irradiated in the Clinton reactor were decanned by puncturing each end of the jacket and placing the brick in a small furnace maintained at a temperature in excess of the melting point of bismuth. Molten bismuth drained from the jacket, leaving the jacket essentially free of radioactive contaminants associated with the bismuth.[35,36] Slugs subjected to more intense

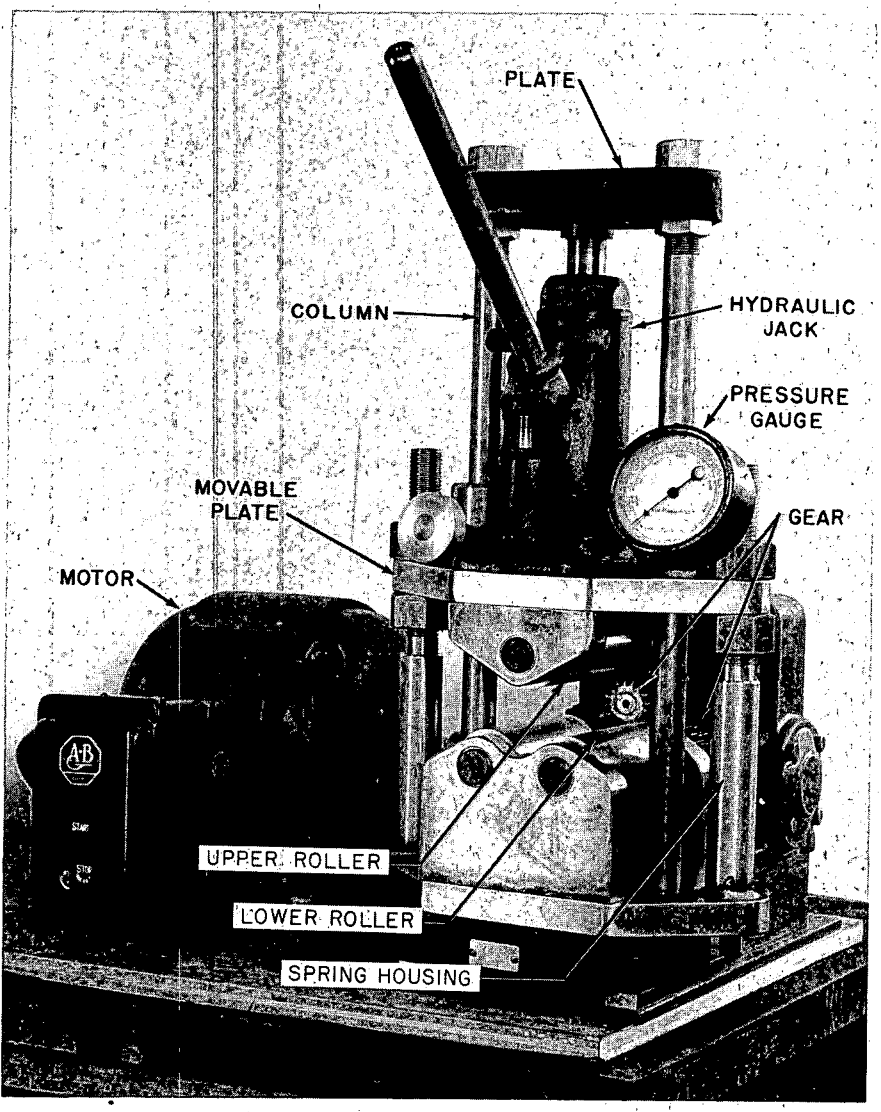


Fig. 7.6 — Mechanical slug-decanning apparatus.

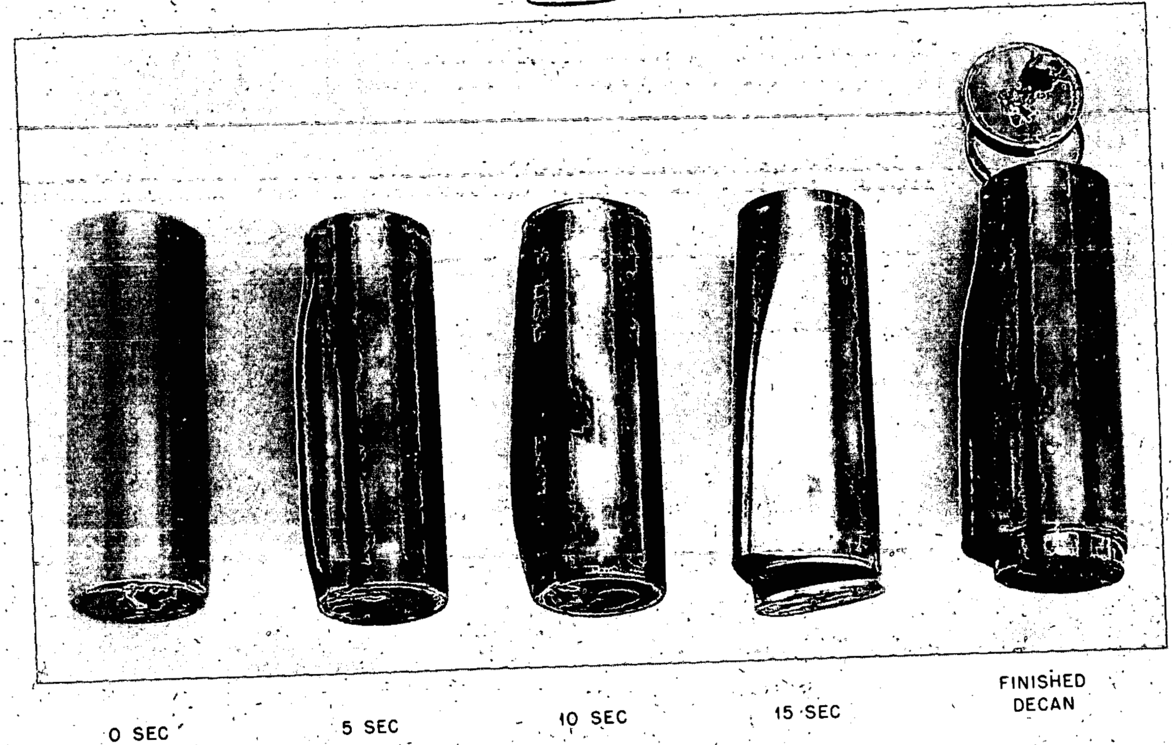


Fig. 7.7—Various stages of mechanical decanning.

irradiation have not been successfully decanned in this manner.[34] When such slugs are subjected to heat (for example, heat from a high-frequency induction heater), a layer of molten bismuth clings to the inside surface of the jacket. This appears to be due to the formation of an alloy (or a mixture of aluminum and bismuth) at the surface between the slug and the jacket during irradiation of the bismuth.

5.4 *Decanning by Caustic.* Aluminum is soluble in caustic solutions, whereas bismuth is insoluble. Consequently jackets may be removed in accordance with the reaction[37]

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

Slugs may be loaded into a basket fabricated from a suitable material (such as stainless steel) and immersed in a dilute solution of caustic soda until the jackets are dissolved. The slugs may be rinsed in water and processed as desired.

An appreciable amount of hydrogen is evolved during this reaction and during the reaction described in Sec. 5.5; hence appropriate measures must be taken to prevent formation of an explosive mixture of this gas.

5.5 *Decanning by Acids.* Aluminum is soluble in a solution containing about 17 per cent hydrochloric acid whereas bismuth is insoluble in this reagent.[37] The equation for this reaction is

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

Slugs may be decanned by immersion in a dilute solution of hydrochloric acid until the jackets have been dissolved, whereupon the slugs may be rinsed and processed as desired.

If irradiated bismuth slugs are to be processed by a wet chemical method, it is convenient to do the decanning operation in the same vessel that is used for the further processing of the slugs (for example, a glass vessel). Care must be exercised in loading slugs into a glass vessel to prevent mechanical damage. One method of protecting the glass during the loading operation is to spread a layer of lime over the bottom of the vessel and to place the slugs on this lime. Water, added slowly to the vessel, will form a slurry with the lime, and as the lime is liquefied the slugs are gently deposited on the bottom of the vessel. The liquid slurry may be withdrawn from the vessel, or acid may be added and the slurry dissolved along with the slug jacket.

Another method of loading may be employed in which a layer of crushed solid carbon dioxide (dry ice) is spread over the bottom of the vessel, and the slugs are placed upon this layer. The solid carbon dioxide may be permitted to evaporate naturally, or the evaporation may be accelerated by heat applied to the vessel or by the addition of water to the carbon dioxide and slugs in the vessel.

The decanning operation may be done in the apparatus[38] shown in Fig. 7.8. This apparatus consists of a glass jar, 12 in. in diameter by 24 in. high, fitted with a cover through which pass fittings connected to a glass heating coil. These fittings serve to introduce a heat-transfer medium, such as Dowtherm A (Dow Chemical Company), into the heating coil to permit the solution in the jar to be heated. A circulating pump with a suitable control mechanism is provided to circulate the hot heat-transfer medium through the glass coil.

Passing through the cover and rigidly attached thereto are one or more glass tubes which are partially closed at the lower end and which extend almost to the bottom of the jar. This lower end is provided with a perforated plug adapted to permit solution to pass through freely and retain solid material of appreciable size. Holes are formed in the vertical tubes about midway of their height, and removable covers are attached to the upper ends of the tubes. The reactor jar is filled with acid solution to a depth slightly above the holes in the vertical tubes, the covers are removed from these tubes, slugs are dropped into the tubes until the upper ends of the slugs are about even with the surface of the solution, and the tube covers are replaced.

The cover is provided with a water-cooled outlet adapted for connection to a vent line, the outlet forming a condenser whereby condensable substances in the vent gas are liquefied and returned to the reactor jar. A water-cooled heat exchanger is fitted to a dip tube so that solution from the jar may be cooled as it is withdrawn.

Hot heat-transfer medium is circulated through the heating coil until the solution reaches the desired temperature which is then maintained by a control mechanism associated with the circulating apparatus. A vigorous reaction occurs around the slugs in the vertical tubes, and gas evolved during the reaction rises in the tube and escapes through the holes in the side of the tubes. This gas acts as a gas-lift pump, drawing fresh solution into the bottom of the tube and discharging the spent solution out of the side holes. Thus the solution in the reaction zone is renewed continuously so that dissolution of the jacket is rapidly effected. The decanned slugs may be subjected to further processing operations without removing them from the reactor.

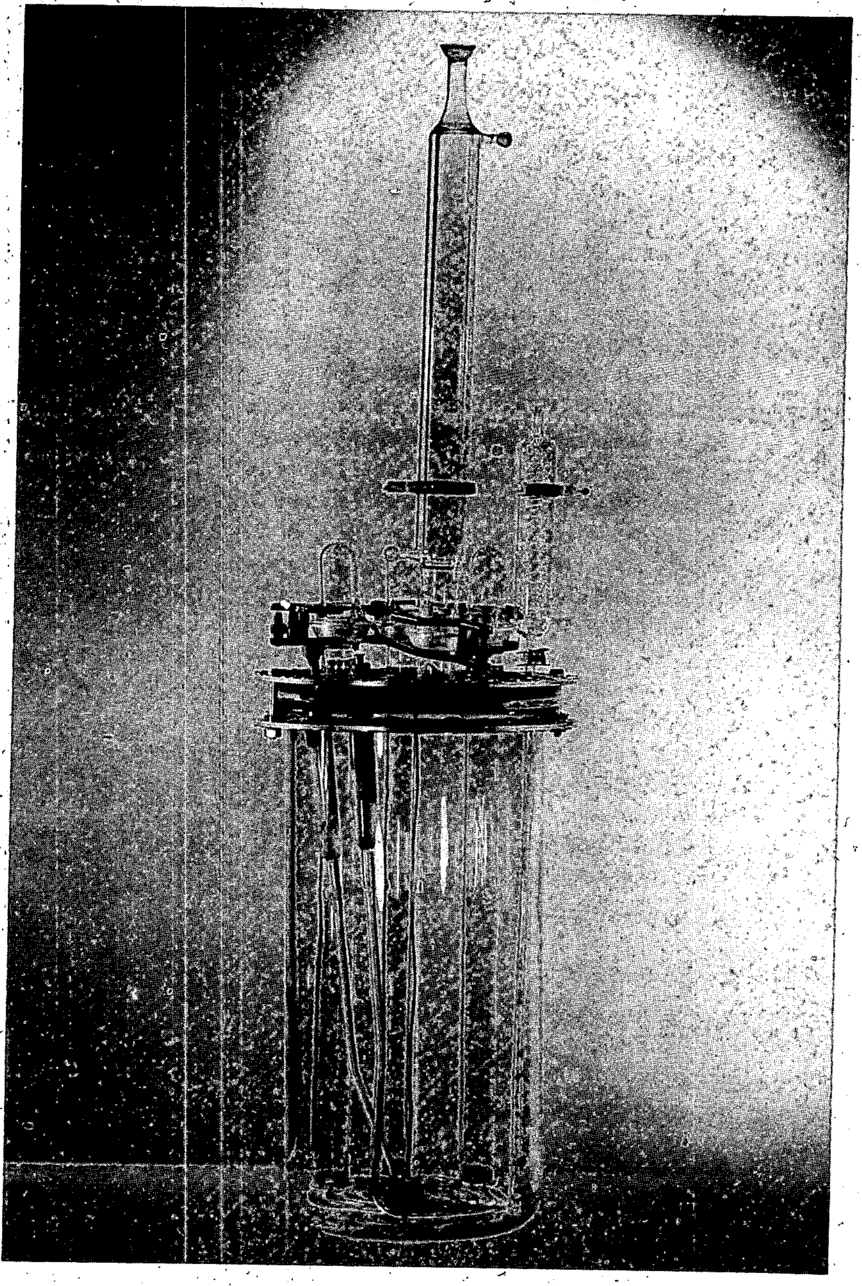


Fig. 7.8—Acid slug-decanning apparatus.

6. DISSOLUTION OF IRRADIATED BISMUTH

6.1 *General.* In order to effect the separation of polonium from irradiated bismuth and other impurities by wet chemical methods, the irradiated bismuth must be dissolved in a suitable liquid from which polonium may be recovered substantially free from impurities. Bismuth is relatively insoluble in most solvents, and special methods are required to effect the dissolution of bismuth in materials from which polonium may be easily recovered.

6.2 *Electrolytic Method.* Irradiated bismuth dissolved in hydrochloric acid is one solution from which polonium may be recovered. Bismuth is not easily dissolved in such a medium, but, if a positive potential is applied to a slug immersed in hydrochloric acid,[39] dissolution can be effected. An apparatus which may be constructed for this purpose consists of an anode compartment, containing hydrochloric acid, which is separated by a barrier from a cathode compartment containing a suitable electrolyte. A bismuth slug is placed in the anode compartment and connected to the positive terminal, or anode, of an electrical circuit. The negative terminal, or cathode, of the circuit is connected to a plate of suitable material (such as carbon) in the cathode compartment. Upon application of the proper potential to the circuit, the bismuth will go into solution in the anode compartment.

The barrier must be constructed of a material such that diffusion of the anode solution into the cathode solution is prevented, and it must be of low electrical resistance so that excessive heat will not be generated by passage of the electrical current required to dissolve the slug. If diffusion of the anode solution into the cathode solution occurs, bismuth will be plated onto the cathode along with any polonium which may be in the solution. Barriers which prevent diffusion of the solutions have an electrical resistance of such a value that considerable amounts of heat are produced as a result of the large electrical currents required to effect rapid dissolution of the slug; hence efficient cooling of the equipment must be provided.

6.3 *Dissolution in Acids.* Irradiated bismuth may be dissolved in a mixture of acids, such as a mixture of hydrochloric and nitric acids. To effect rapid dissolution, the bismuth should be of small particle size in order to offer a large surface area to action of the acid mixture. The large bricks irradiated in the Clinton reactor were melted,[40] and the melt was run into a vessel of water. This procedure resulted in the formation of small bismuth globules resembling shot. The melted bismuth may be run directly into a glass vessel containing concentrated hydrochloric acid, nitric acid is added, and a vigorous reaction occurs. The dissolution of bismuth may be represented by the following reactions:[35]

$$Bi + HNO_3 + 4HCl \rightarrow HBiCl_4 + NO + 2H_2O \tag{7.17}$$

$$Bi + 3HNO_3 + 4HCl \rightarrow HBiCl_4 + 3NO_2 + 3H_2O \tag{7.18}$$

The quantity of nitric acid required is intermediate to that indicated by Eqs. 7.17 and 7.18, the exact quantity being determined by conditions of the reaction. Generally the quantity of nitric acid required will be nearer that indicated by Eq. 7.17 than that indicated by Eq. 7.18. Both reactions occur simultaneously, and it is quite probable that other reactions also occur. Temperature conditions, quantities of reagents, and rates of reagent addition must be carefully controlled to ensure consistent performance.

Polonium probably dissolves in a manner similar to that described above for bismuth; consequently the equations shown for bismuth are assumed to represent the dissolution of polonium.

Bismuth slugs may be dissolved in the same apparatus as is used for the removal of jackets (such as that described in Sec. 5). Each individual apparatus requires different operating procedures and accurate control of process variables. Variables include temperature of solution or reaction, quantities of reagents used, and the rate of addition of reagents.

7. DENITRATION

7.1 *General.* Excess nitric acid in the solution formed during the dissolution operation should be removed or treated in such a manner that it will cause no interference with subsequent operations. The nitric acid may be removed either by evaporating the solution to dryness and heating the residue sufficiently to expel the acid or by the addition of reagents which will combine with the acid and will not combine with other substances in the solution. Preferably, the reagents used for this purpose should form volatile compounds which can be removed readily from the solution.

7.2 *Evaporation of Solution.* The solution from the dissolution operation may be evaporated in steam-heated open vessels which are mounted on electrically heated hot plates. Suitable ventilation hoods are required to carry off the acid vapors produced during the evaporation. Decrepitation[41] occurs when a crust forms over the surface of the solution, resulting in loss of material and contamination of surroundings.

This method of removing nitric acid has the following disadvantages: (1) difficulties in providing an adequate ventilation system for removal of fumes, (2) the large quantities of steam required for heating, (3) the danger of contamination of operating areas, and (4) the hazard to operating personnel.

7.3 *Denitration by Urea.* The digestion solution may be treated by the addition of urea.[42–45] This is not a complete denitration in that only nitrous acid is destroyed whereas the nitric acid is not affected; however, bismuth, one of the reduction-deposition media used in succeeding operations, dissolves very slowly in nitric acid which is free of nitrous acid. Hence the urea treatment allows subsequent operations to be done without major interference by the nitric acid.

The urea treatment has the advantage of not requiring heat.

7.4 *Denitration by Formaldehyde.* Denitration can be effected by raising the temperature of the solution to 85°C and adding formaldehyde. The reaction probably proceeds as

$$HCHO + 4HNO_3 \rightarrow CO_2 + 2N_2O_4 + 3H_2O$$

$$3HCHO + 4HNO_3 \rightarrow 3CO_2 + 4NO + 5H_2O$$

with the first reaction predominating.[46]

The solution should be heated to about 85°C prior to the addition of the formaldehyde because, if the formaldehyde is added to the cool solution, the reaction may become violent when the temperature of the solution is raised. The formaldehyde is added in small portions, and the solution is continuously agitated. The reaction is complete when the evolution of brown fumes ceases.

A disadvantage of the formaldehyde method of denitration is the fact that some polymerization of the formaldehyde occurs. The polymer causes no interference in certain of the alternate subsequent operations; in others it is necessary to periodically remove the polymer.[47]

7.5 *Denitration by Formic Acid.* Formic acid may be used as a denitrating agent through reactions having the same end products as the formaldehyde reactions:[46]

$$HCOOH + 2HNO_3 \rightarrow CO_2 + N_2O_4 + 2H_2O$$

$$3HCOOH + 2HNO_3 \rightarrow 3CO_2 + 2NO + 4H_2O$$

The first reaction predominates.

The treatment may be carried out in the vessel which is suitable for denitration by formaldehyde. The temperature required for a reasonable reaction rate is 90 to 95°C, which is only slightly higher than for the formaldehyde treatment. The end point may be observed by a sharp color change of the solution from orange-yellow to greenish-yellow. There is essentially no difference in the reaction times of the formaldehyde or formic acid denitrations.

8. CONCENTRATION AND PURIFICATION

8.1 *General.* After denitration the polonium is in a 6N to 10N hydrochloric acid solution which is nearly saturated with dissolved bismuth. Three processes, and variations thereof, have been employed to improve the polonium-bismuth ratio. This ratio can be improved by these processes by a factor of approximately 500,000.

The first two described processes, the bismuth process and the silver process, make use of the fact that polonium, being more noble than either bismuth or silver, can be displaced from solution by these materials and deposited upon these materials as the reduced metal. In the tellurium process the polonium is removed from solution by coprecipitation with tellurium by means of a reducing agent.

8.2 *Bismuth Process.* (a) *First Reduction and Deposition on Bismuth.* (1) *General.* Bismuth has the approximate redox potential necessary to reduce ionic polonium without reducing ionic bismuth. One immediately apparent advantage of using bismuth as a reduction and deposition medium is the fact that (using bismuth from the same lot as was used for irradiation) no new impurities are introduced into the process. Only those elements more noble than bismuth will deposit to any degree on the bismuth; hence less-noble-than-bismuth metals are separated by this reduction and deposition process. By maintaining a high normality of chloride-ion concentration (greater than 9N), good separation of silver is also attained.

The rate of deposition of polonium onto the bismuth reduction-deposition medium is a function of the surface area of the bismuth, the speed at which this surface is brought into intimate contact with the solution, the concentrations of interfering impurities, and other factors whose effects cannot be completely evaluated. Considerable work has been done to ascertain optimum particle size, when the bismuth for reduction-deposition is in powder form, and to develop ways of spreading small quantities of the bismuth over large areas.

Four general methods, and variations thereof, of the first reduction and deposition of polonium from a hydrochloric acid solution onto bismuth have been used: (1) agitation reduction-deposition, (2) bed reduction-deposition, (3) flotation reduction-deposition, and (4) column reduction-deposition. The first three methods use finely divided bismuth powder; the fourth method uses bismuth-coated glass rods. An improvement of the polonium-to-bismuth ratio by a factor of about 50 is effected by any of these four methods.

(2) *Agitation Reduction-Deposition.* Agitation reduction-deposition may be accomplished by placing the solution in a glass vessel, adding bismuth powder (150 to 200 mesh), and agitating the slurry by

means of a motor-driven glass-enclosed stirrer. Samples for alpha assay of the solution may be taken periodically to ascertain the completeness of the reaction. The supernatant solution may be withdrawn by means of a dip-line, while the bismuth powder, now containing the polonium, remains in the vessel. Disadvantages of this method are the facts that it is difficult to remove the supernatant solution without also carrying away some of the powder and that the taking of samples for analysis is hazardous.

(3) *Bed Reduction-Deposition.* Bed reduction-deposition may be accomplished by passing the denitrated solution through a vertical piece of glass pipe or glass tubing which contains fine (150 to 200 mesh) bismuth powder held in place by a filter disk or a glass-wool plug. Passage of the solution through the tube may be facilitated by applying a constant vacuum below the bed. The thickness of the bismuth-powder bed will also affect the rate of flow. This method has an advantage over the agitation method in that it may be remotely operated and samplers for alpha-assay may be readily installed on either side of the bismuth. In addition, the filtrate cannot carry away with it some of the powder as is the case with the agitation method. On the other hand, any insoluble material, such as polymers from a formaldehyde denitration, will be filtered out by the bismuth bed and the retaining medium, and prohibitively slow flow rates may result.

(4) *Flotation Reduction-Deposition.* In the flotation reduction-deposition method, the solution is made to flow upward through a tube, Fig. 7.9, causing the bismuth powder which is contained in the tube to be suspended and dispersed throughout the solution.[48] Two or three of these towers may be connected in series, and the flow rate of the solution through these towers should be carefully adjusted to be fast enough to cause the powder in each tower to be suspended and yet slow enough so that the powder is not carried over from one tower to the next. Powder of 200 to 325 mesh is normally used in this apparatus.

(5) *Column Reduction-Deposition.* Investigations of column reduction-deposition of polonium onto bismuth came about somewhat incidentally during the development of the silver process (Sec. 8.3). Attempts to plate bismuth onto silvered glass beads were not successful, but a method was developed for the electrodeposition of bismuth onto silvered glass rods. These rods were placed in a glass column through which the active solution flowed. Deposition of the polonium onto these rods was substantially complete after about three passes of the solution through one column or one pass through three columns in series; however, some difficulty was encountered in removing the bismuth and the polonium from the rods.

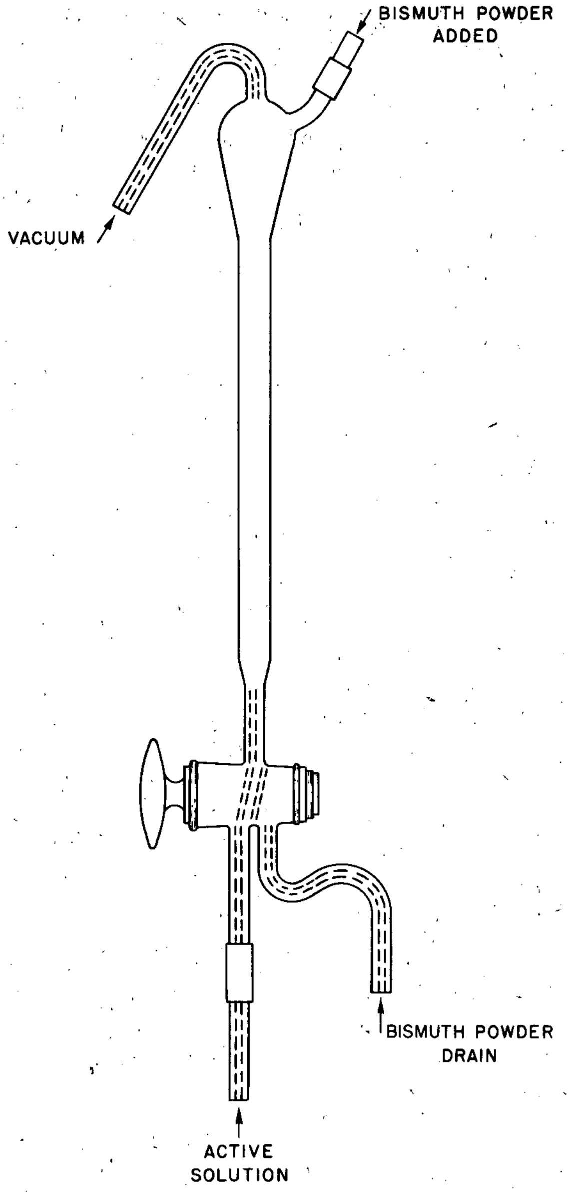


Fig. 7.9 — Flotation reduction-deposition apparatus.

(b) *Dissolution and Denitration.* The end product from any of the four described reduction-deposition methods is very similar in composition to the original unjacketed bismuth slugs except that the amount of bismuth has been reduced by approximately a factor of 50, and some separation of less-noble-than-bismuth metals has been effected.

The bismuth powder may be dissolved as described in Sec. 6.3, and this solution may then be denitrated by any of the methods described in Sec. 7. The amounts of reagents necessary, both in dissolution and in denitration of the powder, are considerably reduced from the amounts required for the slugs, owing to the smaller amount of material involved.

(c) *Second Reduction and Deposition on Bismuth.* A second reduction-deposition operation, similar to that described in Sec. 8.2a, further improves the polonium-to-bismuth ratio as well as effecting further separation of less-noble-than-bismuth metals. In addition, maintaining a high chloride-ion concentration in the solution keeps much of the silver in solution. By using approximately $\frac{1}{100}$ as much bismuth in this second reduction-deposition as is used in the first reduction-deposition, the polonium-to-bismuth ratio is improved by a factor of approximately 100.

Agitation reduction-deposition may be performed in an identical manner to that described for the first reduction. Smaller size equipment may be employed as a result of the decrease in the amount of bismuth powder to be used. Agitation of the slurry by means of a motor-rotated stirrer has been used, and, in addition, gas agitation has been successfully employed.[49,50] Bubbling a gas such as carbon dioxide through the solution serves not only to suspend and stir the powder but also to remove any dissolved oxygen.

Bed reduction-deposition may likewise be performed by a method identical to that described for the first reduction. If it has been determined that the volatilization step, described in Sec. 8.2d, is to be used, it is desirable that the vessel in which the powder is placed, and through which the solution flows, be suitable for use in the volatilization step.[51] This eliminates the necessity of moving the powder from one container to another. Figure 7.10 shows a porcelain crucible which is suitable for bed reduction-deposition and for volatilization.

(d) *Volatilization.* The bismuth powder, from any of the reduction-on-bismuth methods, is normally further purified by one of two alternate methods: (1) volatilization or (2) reduction with stannous chloride. The stannous chloride step is described in Sec. 8.2e.

The volatility of polonium was observed by early workers, and advantage was taken of this property during concentration and purification studies (Chap. 2, Sec. 3.1c). Some effort at Mound Laboratory has been directed toward the utilization of distillation as a means of separating polonium from irradiated bismuth. The work on distillation is described in Chap. 8.

The removal, by volatilization, of polonium from platinum foils onto which it had been electrodeposited (Sec. 9) has been widely used because some platinum usually came off with, and hence contaminated, the polonium if removal were effected by chemical stripping.[52] This procedure led to the use of volatilization as a means of further separating polonium from bismuth.

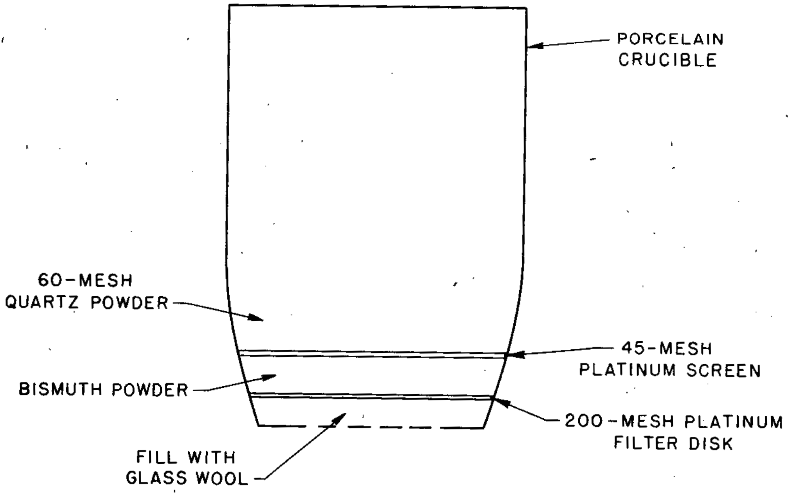


Fig. 7.10—Crucible suitable for both bed reduction-deposition and volatilization.

Volatilization of polonium from a crucible, such as the one shown in Fig. 7.10, may be carried out in a quartz volatilization tube and an electric furnace similar to those shown in Fig. 7.11. The crucible may be the one in which the bed reduction-deposition was carried out; if agitation reduction-deposition was used, the powder will have to be transferred to a vessel which will fit the volatilization tube.

It is necessary to wash the bismuth powder free of all chloride ions since volatilization is ineffective in removing certain metallic impurities if present as chlorides. An effective wash is hydrochloric acid followed by distilled water.

The crucible containing the washed powder is carefully transferred to the volatilization tube which is then inserted into the furnace. The volatilization tube is equipped with a cover which has a connection by means of which the tube may be evacuated. The powder is heated for a few minutes under vacuum, at a temperature of about 150°C, in order to dry the powder. The system is then vented to pure oxygen, and the temperature is raised to about 650°C and held there for a few minutes.

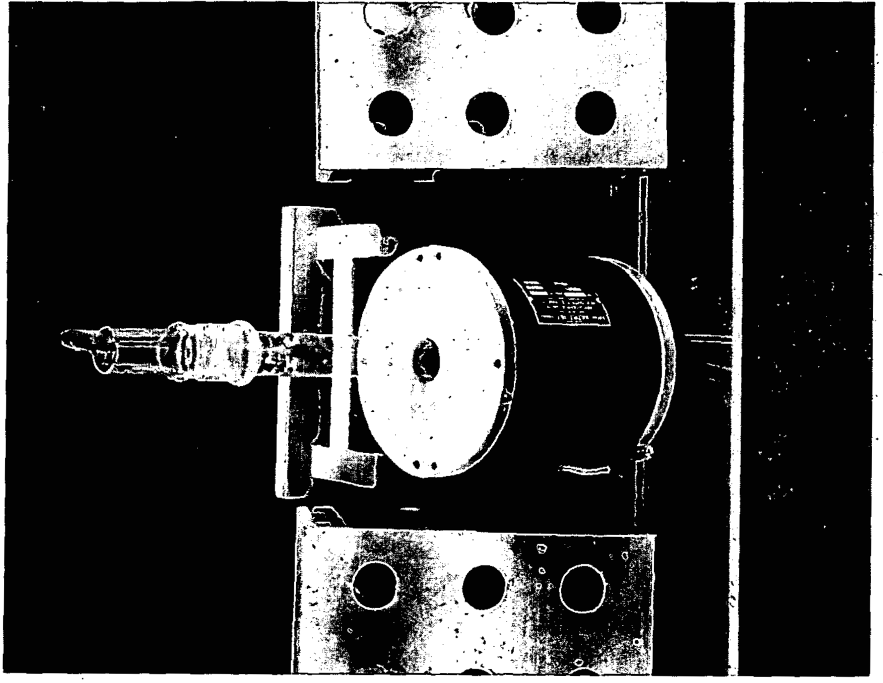


Fig. 7.11—Volatilization tube and furnace.

This step converts the bismuth (melting point 271°C) to bismuth oxide (melting point 820°C) and the polonium to polonium dioxide. (This oxidation is performed for two reasons: (1) metallic polonium is not readily volatilized from the molten bismuth, and (2) the vapor pressure of the bismuth is materially reduced by conversion to the oxide. Furthermore, polonium dioxide decomposes readily at the temperatures and pressures used, and the metallic polonium readily vaporizes from the bismuth oxide if the volatilization temperature is kept below the melting point of the bismuth oxide.) The pressure in the volatilization tube is then reduced to about 100 μ, and the temperature is raised to 800°C. Under these conditions the polonium will be removed from the bismuth in 30 to 60 min, depending upon the size of the batch being processed. The polonium deposits as a metallic ring around the inside of the cool end of the volatilization tube. Approximately 1 per cent of the bismuth will volatilize along with the polonium; thus this step represents a further improvement in the polonium-bismuth ratio of about 100.

(e) *Reduction with Stannous Chloride.*[38] The reduction of polonium with stannous chloride is a concentration-purification step alternate to the volatilization step. The solubility of polonium in most solvents is low,[53] and a purification step based upon the precipitation of polonium from a solution containing the impurities, rather than the reverse procedure, seemed feasible. Stannous chloride was recognized by early workers[54–58] as an effective reagent for separating polonium from solutions. Stannous chloride has a particular advantage as a reducing agent for polonium; it is a solution in either its oxidized or reduced state, and hence metallic polonium may readily be filtered and washed free of it.[53]

The bismuth powder from any of the reduction-deposition methods may be dissolved as described in Sec. 6.3 and the solution denitrated as described in Sec. 7. The powder may also be dissolved in a mixture of concentrated hydrochloric acid and hydrogen peroxide. The excess peroxide should be destroyed by boiling. Addition of a 10 per cent stannous chloride solution to the polonium solution will reduce the polonium to a finely divided black powder. Agitation facilitates this reduction and may be accomplished by bubbling nitrogen through the solution or by boiling the solution. After a short time the finely divided suspension will coagulate, and the solution may be filtered. The precipitate is then washed with a 1 per cent stannous chloride solution followed by a wash in distilled water to remove the bismuth and tin ions still with the polonium.

(f) *Precipitation with Ammonium Hydroxide.* Reduction-deposition processes separate polonium from those metallic impurities less noble than bismuth. The bismuth is further separated from the polonium in either the volatilization or the reduction-with-stannous chloride step. It is still necessary to separate those elements which are more noble than bismuth. These would plate out with the polonium in the ensuing electrodeposition operations (Sec. 9) which represent the final purification of polonium. Silver is generally the chief impurity at this point; it can be separated from the polonium by precipitating the polonium with ammonium hydroxide, the silver remaining in solution as the ammonium complex. Other complexing agents may be added at this point for the removal of other noble impurities if they are present. For example, potassium cyanide will act as a complexing agent for gold, and hydrogen peroxide will reoxidize any metallic gold which might precipitate at this point.[53]

The volatilized polonium (if the volatilization step was used) in the volatilization tube may be dissolved by carefully pouring nitric acid down the sides of the tube; refluxing may be necessary to completely dissolve the polonium. The washed polonium from the stannous chloride step (if this step was used) may also be dissolved in nitric acid, although a mixture of concentrated hydrochloric acid and hydrogen peroxide is somewhat more effective. (The excess hydrogen peroxide in the solution must be decomposed prior to the addition of ammonium hydroxide.)

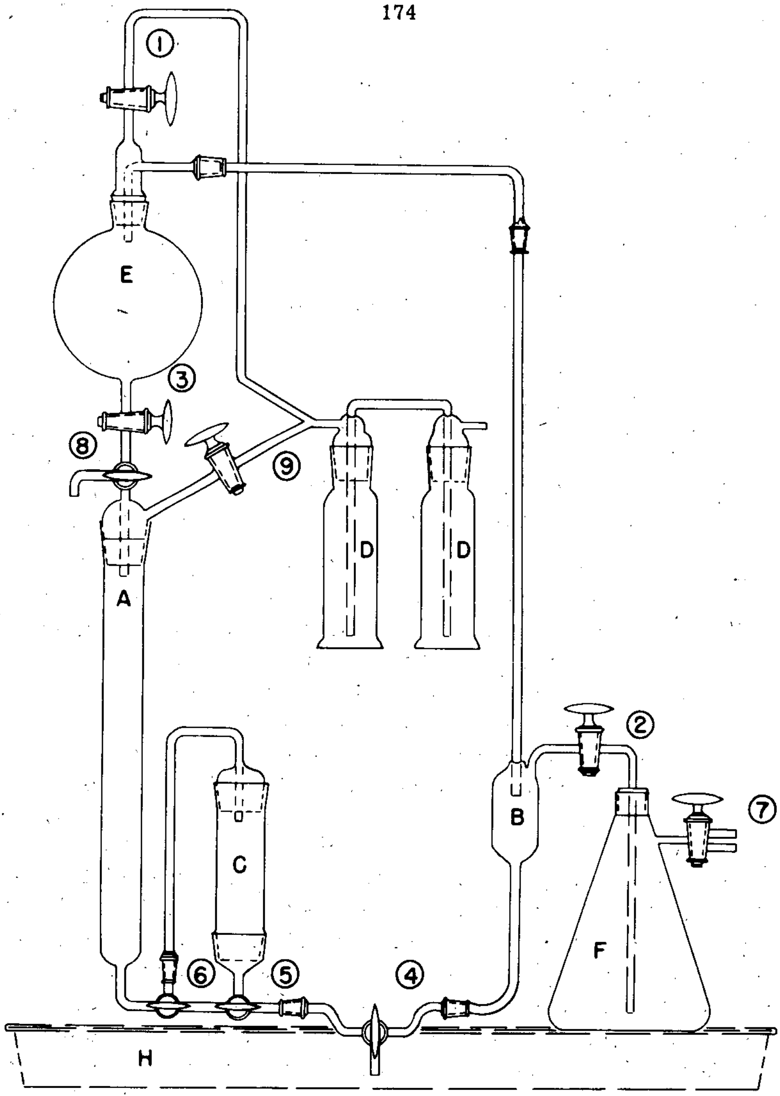
Ammonium hydroxide may then be added to the nitrate or the chloride solution (whichever it happens to be), and polonium will precipitate as the hydroxide. Boiling will aid in coagulating the precipitate. The precipitate is filtered and is then washed several times with ammonium hydroxide and then with distilled water. The precipitate may now be dissolved in whatever medium is desired for electrodeposition (Sec. 9).

8.3 *Silver Process.*[59] (a) *Reduction-Deposition.* The spontaneous deposition of polonium on silver has been used by several investigators[60–63] as a convenient method for separating polonium from other elements. Reduction-deposition on silver will accomplish good separation of the polonium and bismuth because silver is more noble than bismuth, and the bismuth will not be reduced by the silver. The separation of the polonium from the silver on which it was deposited will also effect separation of the troublesome radioactive silver impurity (Sec. 2.9).

The silver process may be used with the denitrated solution of the irradiated bismuth slugs as the starting material. This solution can be circulated through an apparatus such as is shown in Fig. 7.12. The apparatus consists chiefly of column A (packed with silvered glass beads) through which the solution may be circulated by means of a carbon dioxide–operated gas lift. Silver-coated glass wool, silver leaf, and fine silver powder have also been used in such columns.[64,65] The beads may be silvered by first roughening the beads and then silvering them by Brashear's method[66] (the reduction of ammoniacal silver solution with glucose). It is necessary to roughen the beads to prevent stripping of the silver by the hydrochloric acid solution containing the polonium.

The solution is circulated through the column as many times as are necessary to remove the polonium. The depletion of the polonium from the solution may be determined by alpha counting a sample of the solution.

Ferric ions present in the solution cause considerable trouble by stripping the silver from the beads, and attempts to keep these ions reduced to the ferrous state have not been too successful. Stannous chlo-



A. Reduction-deposition column
B. Gas lift
C. Adsorption column
D. Exhaust traps containing HCl
E. Solution reservoir
F. Trap for gas lift
H. Enameled pan

Stopcocks

1. Vent for reservoir
2. Gas-lift pressure control
3. Solution inlet
4. Inlet for active solution and washes and drain for apparatus
5 and 6. Bypass for adsorption column
7. Gas control for gas lift
8. For measuring flow rate
9. Vent for column

Fig. 7.12—Silver-process apparatus.

ride will keep the iron reduced, but it also reduces silver chloride if the silver chloride is present in too high a concentration.

(b) *Dissolution of Silver and Polonium.* The silver coating, upon which the polonium is deposited, is best dissolved off the glass beads by refluxing two portions of 7.5N nitric acid in the column for about 30 min each, followed by a similar refluxing with 6N hydrochloric acid and one with distilled water. Filling the column with concentrated hydrochloric acid and allowing it to stand overnight assures the dissolution of all the silver and the polonium.

The silver can also be dissolved off the beads by passing chlorine gas over the beads, which have been previously wetted with ammonium hydroxide, and then passing concentrated ammonium hydroxide over the beads several times.

(c) *Separation of Silver and Polonium.* If the silver has been dissolved in ammonium hydroxide, the polonium may be separated from this solution by passing the solution through an adsorbing medium, such as alumina, which is placed in column C of Fig. 7.12. Three passes of the solution are generally sufficient to remove almost all the polonium. The polonium may then be removed from the adsorbent by elution with hydrochloric acid. Mixtures of 50 per cent Celite (Johns-Manville) and magnesium carbonate, barium carbonate, or calcium carbonate are also effective adsorbing media.

If the silver has been dissolved in acids, these acids are neutralized with ammonium hydroxide. Polonium precipitates as the hydrated oxide, and silver remains in solution as the complex ammonium ion. Separation may be effected by filtering through a sintered-glass filter. The hydrated oxide of polonium may be dissolved in whatever medium is desired for electrodeposition (Sec. 9).

8.4 *Tellurium Process.*[67] (a) *Coprecipitation of Tellurium and Polonium.* The tellurium process, like the silver process, has been used either with the denitrated solution of the bismuth slugs or with the denitrated solution of the bismuth powder from the primary reduction-deposition on bismuth as the starting material.

The coprecipitation of polonium and tellurium was reported by Marckwald[54] who reduced the two materials in a hydrochloric acid solution by means of stannous chloride. This is the first step in the tellurium process.

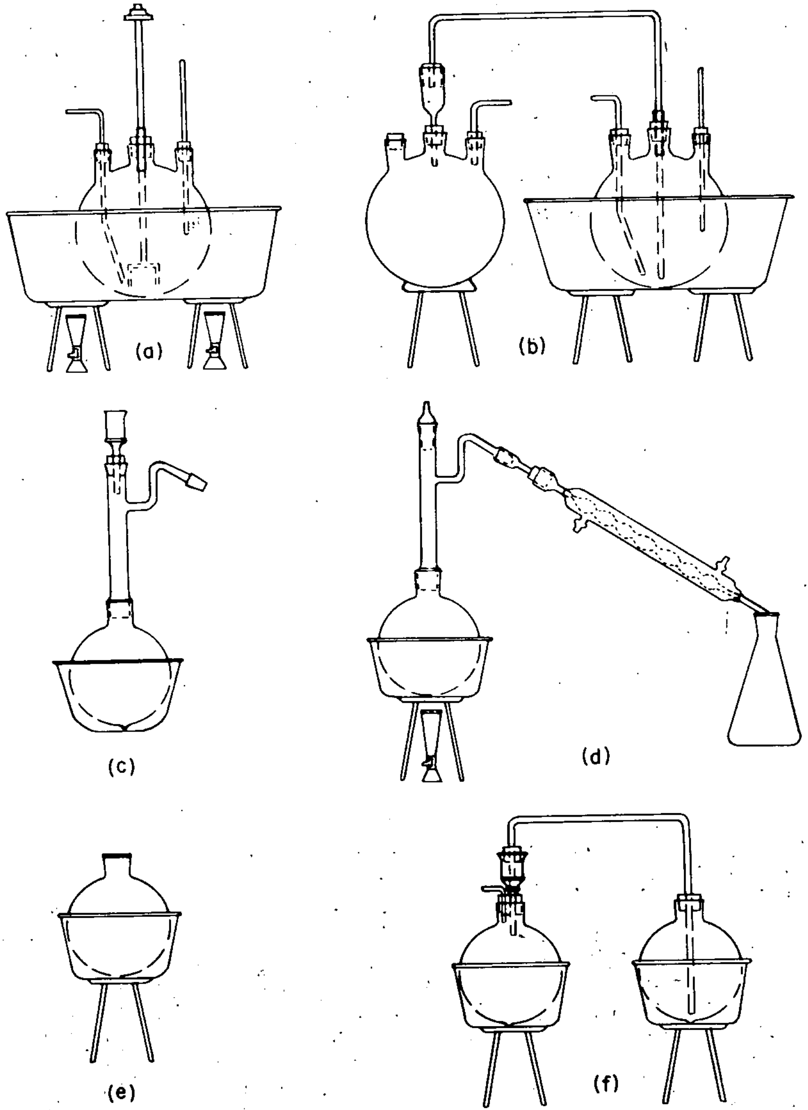
Telluric acid and stannous chloride are added to a denitrated solution of bismuth which contains polonium. The solution is then heated until the tellurium precipitates and coagulates; the polonium is precipitated with the tellurium (Fig. 7.13a). Agitation of the solution by means of a stirrer is helpful. (Hypophosphorous and hydrosulfurous acids have also been used as reducing agents, but the results using these reagents were not as good as those obtained with stannous chloride.) The solution is filtered, and the precipitate is washed with hydrochloric acid (Fig. 7.13b). The precipitate is then dissolved (Fig. 7.13c) in aqua regia, and the solution is denitrated (Fig. 7.13d) as described in Sec. 7.

(b) *Reprecipitation of Tellurium and Polonium.* It has been found[68] that the amount of bismuth precipitated by a given weight of tellurium in the tellurium-polonium precipitation is a function of the concentration of the bismuth. If the starting material for the tellurium process is the denitrated solution from a bismuth reduction-deposition operation, the bismuth concentration is so small that the amount precipitated is not harmful. However, if the starting material is the denitrated solution from the dissolution of bismuth slugs, the amount of bismuth precipitated is so great that a separation must be made. This can be accomplished by reprecipitating the tellurium and the polonium.

The reprecipitation is carried out in the same manner as the first precipitation except that the precipitate, following filtration, is washed with hydrochloric acid to which has been added a reducing agent such as hypophosphorous acid. This is necessary to prevent loss of a considerable amount of polonium in the hydrochloric acid wash. The difference between the behavior of the polonium in the washing operation of the first precipitation (no loss of polonium occurs) and the washing operation of the second precipitation (considerable loss of polonium occurs) may be explained as follows: In the first precipitation the tellurium is added as telluric acid. In the second precipitation the tellurium is probably in the form of tellurous acid since it seems improbable that a solution which is obtained by dissolving tellurium in aqua regia, and which is then denitrated, could contain any telluric acid. The tellurium formed by reduction of the tellurous acid contains some hydrochloric acid–soluble tellurium, probably tellurium dioxide. Any polonium oxide formed in a manner similar to the formation of the oxide of tellurium will also be lost in the hydrochloric acid wash. Laboratory experiments have confirmed the fact that this phenomenon will occur when tellurous acid rather than telluric acid is used.[68]

The precipitate from the reprecipitation operation is handled (following the wash) by a procedure identical to that used for the precipitate from the original precipitation operation.

(c) *Separation of Silver.* A separation of silver, which will also precipitate with tellurium and polonium, may be necessary, depending upon the silver content of the starting material and the allowable silver content of the final product. If such a separation is to be made, the



(a) Coprecipitation of tellurium and polonium
(b) Filtration and washing of tellurium and polonium
(c) Dissolution of tellurium and polonium
(d) Denitration of tellurium and polonium by evaporation
(e) Precipitation of tellurium
(f) Separation of tellurium

Fig. 7.13—Diagrammatical representation of the tellurium process.

starting material is the aqua regia solution of the precipitate from the first precipitation (or the second precipitation, if it is used) of tellurium and polonium.

To this aqua regia solution is added an excess of ammonium hydroxide and a little hydrogen peroxide. The tellurium precipitates (probably as tellurium dioxide, formed by the action of hydrogen peroxide), and the polonium precipitates with the tellurium. The silver remains in solution as the ammonium complex. The solution is filtered, and the precipitate is washed with ammonium hydroxide. The precipitate is then dissolved in hydrochloric acid.

(d) *Separation of Tellurium.* The hydrochloric acid solution of tellurium and polonium, from either precipitation of tellurium and polonium or from the silver separation, is the starting material for the final step of the tellurium process, the separation of the tellurium.

Hydrazine dihydrochloride is added to the tellurium-polonium solution, and the mixture is heated under reflux conditions. The reduced tellurium will precipitate and coagulate (Fig. 7.13e); the polonium will remain in solution; separation may be effected by filtration (Fig. 7.13f). The solution can then be converted to whatever medium is desired for electrodeposition.

Formic acid, oxalic acid, hydroxylamine hydrochloride, thiourea, and sodium thiosulfate have all been tried as reducing agents in this step of the process. None of these reducing agents is as effective as hydrazine in this process.

8.5 *Factors Affecting the Choice of Operational Procedures.* It should not be deduced that one of the described processes should be used in its entirety to the exclusion of all operations in the other processes. For example, it has been pointed out that both the silver and the tellurium processes have been used with the denitrated solution of bismuth slugs as a starting material and also with the denitrated solution of bismuth powder from a reduction-deposition on bismuth as a starting material. Likewise, many other variations of procedures of all the processes are possible.

Several factors would affect (to varying degrees) the exact procedure used to chemically separate polonium from irradiated bismuth. The equipment available will influence the decision as to which separation procedure will be used. The purity of the irradiated bismuth may affect the choice of procedure. At one time silver was a very troublesome impurity, and much effort was directed toward perfecting methods of separating it from solution during processing. Such separation methods were achieved; however, at about the same time, the silver content in the original bismuth was reduced to a level such that some of the purification from the standpoint of silver depletion might not have been necessary.

The most important factor affecting the choice of operational procedures is the purity requirement of the polonium. This may vary widely depending upon the intended use of the polonium. The omission of any step, or steps, designed to remove a particular impurity which is not objectionable in the final product will simplify the recovery of the polonium.

9. ELECTRODEPOSITION[69]

9.1 *General.* The electrodeposition of polonium from a solution onto a metallic electrode represents the final step in the separation and purification of polonium. In addition to the further purification which can be attained by electrodeposition, the polonium will be in a solid metallic form which is much easier to handle than is a solution. The purity (weight) of the polonium after electrodeposition can approach 98 to 100 per cent.

Spontaneous deposition of polonium onto copper and onto nickel electrodes has been used (Chap. 1, Secs. 3 and 4.2) as a method of final separation of polonium. Electrodeposition has been in use since early in 1944. The solution-cathode potential was at first manually controlled; automatic controllers (Chap. 9, Sec. 4.4) which will control the solution-cathode potential for four simultaneous plating operations are presently in use.

The electrodeposition of polonium has been, and can be, done on many different materials and can be done on either the anode or the cathode of the electrodeposition apparatus. Likewise, electrodeposition can be done from many different media, both acidic and basic. The choice of media and material will usually depend upon the ultimate use of the polonium.

9.2 *Deposition from Nitric Acid.* Nitric acid is a satisfactory medium for the plating of high concentrations of pure polonium. It has been investigated more thoroughly than any other medium.

The electrodeposition of polonium from nitric acid can be done in a beaker such as the one shown in Fig. 7.14. Two cathodes, made of platinum gauze, are suspended between two platinum anodes. The solution is stirred by means of a glass-enclosed iron bar which lies on the bottom of the beaker, and this bar is rotated by a rotating magnetic field beneath the beaker. Leads from the anodes, the cathodes, and the normal calomel electrode are attached to an automatic controller (Chap. 9, Sec. 4.4) which maintains a constant solution-cathode potential. Plating is normally done at 0.0 volt with respect to the normal calomel electrode; 1.5N nitric acid is quite satisfactory for this operation.

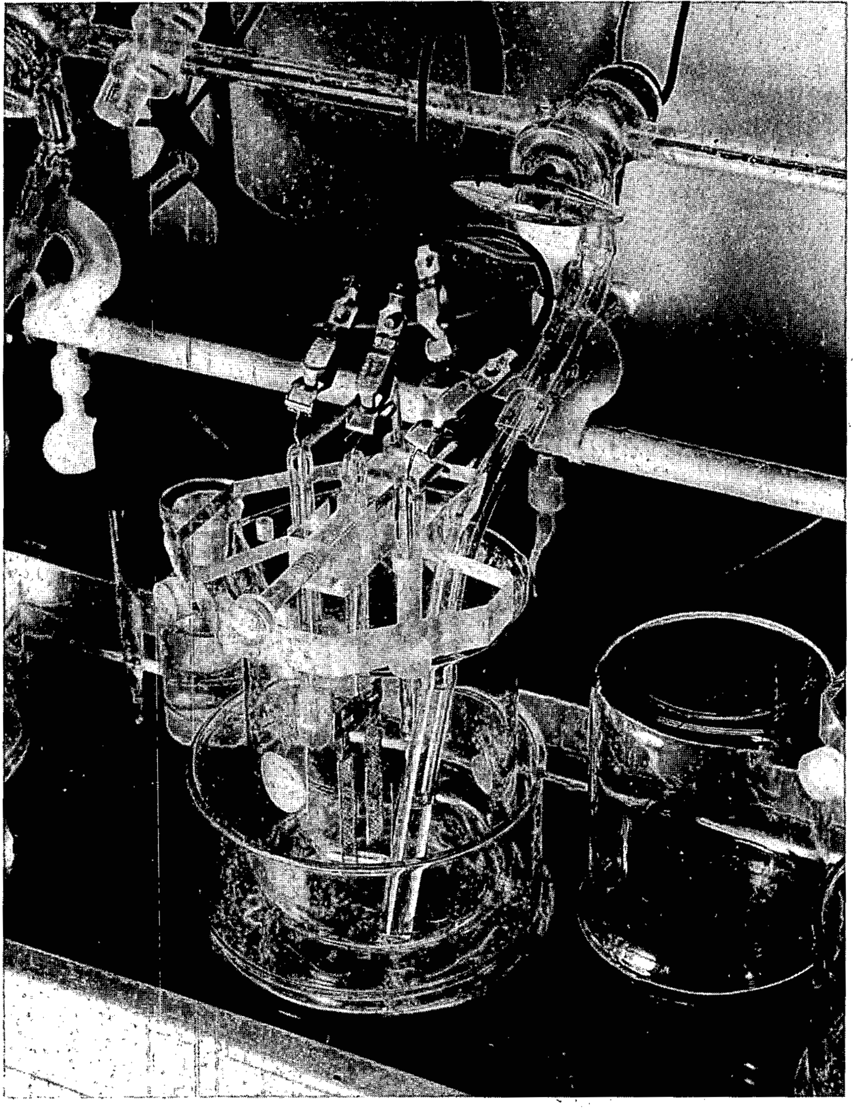


Fig. 7.14—Electrodeposition apparatus.

Deposition may be done on cathodes fabricated of gold, provided that platinum anodes are used. Gold anodes dissolve and will deposit onto the cathodes along with the polonium. Deposition has also been done on tantalum, molybdenum, carbon, and, under certain conditions, nickel electrodes.

Depletion of the polonium from a solution is more rapid if a gauze is used for the cathode, rather than a solid foil.

Polonium oxidizes readily, and the plated foil or gauze must be protected from air. This may be done by keeping the material immersed in a solution such as acetone, petroleum ether, or absolute alcohol, or the foil may be sealed in an inert atmosphere.

9.3 *Deposition from Other Inorganic Acids.* Deposition can be effected from a hydrochloric acid solution, although special precautions must be taken. For example, platinum anodes dissolve in the solution with subsequent deposition on the cathode along with the polonium. The quantity of platinum which dissolves increases with increasing acidity and current density. Graphite anodes are satisfactory provided they have been bonded to prevent flaking and have been treated to prevent the absorption of polonium. Bonding of this type of anode may be accomplished by exposing the graphite to a 1N hydrochloric acid solution and an electrolyzing current of 5 ma for about 1 day. The absorption of active solution by the graphite anodes can be prevented by soaking the anode in a hot kerosene-paraffin solution, removing the kerosene with lead-free gasoline, and then soaking the anode overnight in 6N hydrochloric acid to remove organic solvents.

Some electrodeposition of polonium has been done from sulfuric acid solutions. The solubility of polonium in 1N sulfuric acid is low, and the quality of the deposits is low. Good polonium-plated electrodes may be obtained from a sulfuric acid solution to which some citric acid is added. The addition of the citric acid increases the amount of polonium dissolved.

Hydrofluoric acid works very well as an electrodeposition medium. Smooth adherent deposits can be prepared, up to a density of about 30 curies of polonium per square centimeter. Good separation of polonium and bismuth is possible; the deposition potentials for bismuth and polonium in 1N hydrofluoric acid appear to differ by almost 1 volt. Lucite, polystyrene, or polyethylene beakers should be used in this electrodeposition process; however, it is possible to use standard micropipettes for assaying the solution for its polonium content, provided that the pipettes are immediately and thoroughly rinsed with nitric acid. Satisfactory pipettes have also been made from polystyrene tubing.[70]

The number of neutrons emitted (per unit foil area) from foils plated from hydrofluoric acid is usually greater than the number of neutrons emitted from foils plated from other media; however, some work[70] indicates that very careful operational and handling techniques will keep the neutron emission of foils plated from hydrofluoric solutions comparable to the neutron emission of foils from other plating solutions.

Only a few attempts have been made to plate polonium from perchloric acid. The behavior, in general, of perchloric acid is similar to sulfuric acid; it is difficult to get the polonium into solution. Long plating times and poor deposits characterize perchloric acid plating solutions.

Unmodified solutions of phosphoric acid were not satisfactory for plating because polonium precipitated out of solutions whose acid concentration was as high as 4M. The addition of either citric or oxalic acid increased the solubility of polonium, and smooth adherent deposits could be obtained.

9.4 *Deposition from Organic Acids.* Attempts have been made to electrodeposit polonium from aqueous solutions of the following organic acids: oxalic, tartaric, citric, and acetic. In general, the plating times are long, and the deposits are rather porous. Fairly satisfactory deposition can be made from citric acid solutions onto nickel electrodes.

9.5 *Deposition from Alkaline Solutions.* Sodium hydroxide and sodium cyanide solutions have been tried as electrodeposition media. Good deposition can be obtained, although the plated deposit is no better than that obtained when plating polonium from nitric acid. One disadvantage resulting from the use of these alkaline solutions is the slow rate of deposition.

10. QUANTITY ASSAY

10.1 *General.* Frequent assays in the purification of polonium process are necessary in order to determine the progress of certain reactions, to determine the quantity of activity for material balances, and to determine the polonium content of a final product solution or plated foil. Both the alpha emission and the gamma emission of polonium have been utilized for assay purposes. Polonium has a half life of 138.4 days (Chap. 2, Sec. 2), and the loss of polonium due to radioactive decay must be taken into account in any assay determination. The decrease in the quantity of polonium that is attributable to decay is of the order of 3 per cent per week.

10.2 *Assay by Alpha Emission.* Polonium emits a 5.298-Mev alpha particle (Chap. 2, Sec. 3.1a) which is usable for quantity assay purposes. Solutions of polonium can be sampled (the sample diluted if necessary), mounted on a glass or metal slide, dried, and counted in standard commercially available alpha-counting instruments. The counting range of such instruments may cover an activity range of 0 to 300,000 counts/min at a nominal particle-counting geometry of 50 per cent. In addition to such standard instruments, special low-geometry attachments have been devised at the Dayton Project and at Mound Laboratory which will allow alpha-particle counting to be done directly on samples whose activity is as great as 10^{13} dis/min. These attachments are described in Chap. 9, Sec. 3.1. Techniques for the mounting of radioactive samples and a summary description of the instruments available at Mound Laboratory have been presented by Dauby.[71]

An assay by the sampling of a solution is a very convenient method of following the depletion of a solution by electrodeposition. For the assay of plated foils calorimetric techniques are useful because the entire sample can be inserted into a calorimeter which will measure the quantity of heat produced by the radioactive decay of the sample. Calorimeters are available which will measure alpha-particle-emitting samples covering a wide range of activity. A complete discussion of calorimetry principles, as used at Mound Laboratory, is given in Chap. 10.

10.3 *Assay by Gamma Emission.* Polonium has associated with its radioactive decay a 0.8-Mev gamma ray (Chap. 2, Sec. 3.2) which has been used in certain assay procedures. Gamma-radiation assays may be as accurate as alpha-particle assays; however, it may be somewhat difficult to maintain a constant counting geometry in many instances. Any radioactive silver associated with the polonium may cause incorrect assays, although with proper care assays can be carried out in the presence of this contaminant (Sec. 4.3). Nevertheless, gamma-radiation assays are very useful for rapidly obtaining information which is reasonably accurate, although they are not generally used at Mound Laboratory for a final product assay.

A gamma-radiation assay is particularly useful for monitoring a solution in, for example, a reaction vessel or a reduction-deposition tower, where the taking of a sample for an alpha-particle assay is inconvenient (if not impossible). A gamma-ray-sensitive detector, such as a radioelectric cell (Chap. 9, Sec. 3.2), may be placed in proximity to a vessel which contains the solution to be monitored, while the indicating unit may be remotely located. Radioelectric cells may be designed in a variety of configurations in order that assays may be performed during the course of a particular process without in any manner interfering with the continuation of the process. Constant assay geometries and the attendant constant assay accuracy can be attained through the use of radioelectric cells.

Geiger-Mueller tubes are not as suitable for such an installation because they are more sensitive to small changes in geometry than are radioelectric cells.

A four-input gamma counter (Chap. 9, Sec. 3.4) and a rotating-source gamma counter (Chap. 9, Sec. 3.5) both have been used for the gamma assay of plated foils or gauzes prior to a final assay in a calorimeter. At the present time the radioelectric-type counter is used almost exclusively for this assay because of its inherent stability, accuracy, and ease of operation. Such a preliminary gamma-radiation count provides information for adjusting the calorimeter so that it will operate nearly at balance (Chap. 10, Sec. 3.4). Any discrepancy between the amount of polonium indicated by a final gamma-radiation count and that indicated by a calorimetric measurement might mean that the polonium is contaminated with radioactive silver.

11. QUALITY ASSAY

11.1 *General.* One of the first problems associated with the purification of polonium was the development of a satisfactory method for determining the purity of the polonium on the plated foil or gauze. The purity to be expected of polonium plated from a given solution can be determined through the following procedure:

1. Weigh a small foil.
2. Plate polonium onto this foil from an aliquot of the solution in question under conditions which duplicate as nearly as possible those conditions under which the final plating will be done.
3. Reweigh the foil, determining the quantity of material which was plated.
4. Measure the alpha radiation from the plated deposit.

The relation between the weight and the alpha activity of the deposit will indicate its purity.

The quantity of alpha radiation can be measured calorimetrically or by counting; counting is generally preferable because it is more rapid.

The detection of gamma-ray-emitting impurities associated with the polonium solution (or plated foils) was discussed briefly in Sec. 10.3. A neutron count may also be made on the final foil, or gauze, to detect light-element impurities.

11.2 *Determination of Purity.* Satisfactory determination of the purity, with respect to polonium, of a solution from which the polonium is to be electroplated can be made by plating and analyzing a small percentage of this solution.

The polonium content of a small sample of this solution is depleted by the use of apparatus similar to that shown in Fig. 7.15. A weighed small foil (microfoil) of the same material that is to be used for the final plating is plated in this apparatus. The microbeaker is rotated to effect stirring the solution. Plating conditions (solution-cathode potential, cathode and anode materials, etc.) must be kept identical to those conditions which will be maintained for the plating of the solution proper. Reweighing the microfoil following the plating operation will give the weight of the material which has been deposited on the microfoil. Weighings are done on a quartz-fiber microbalance as described in Chap. 9, Sec. 4.2.

The alpha activity associated with the deposit may be conveniently measured in a special low-geometry alpha counter (Logac-L) as de-

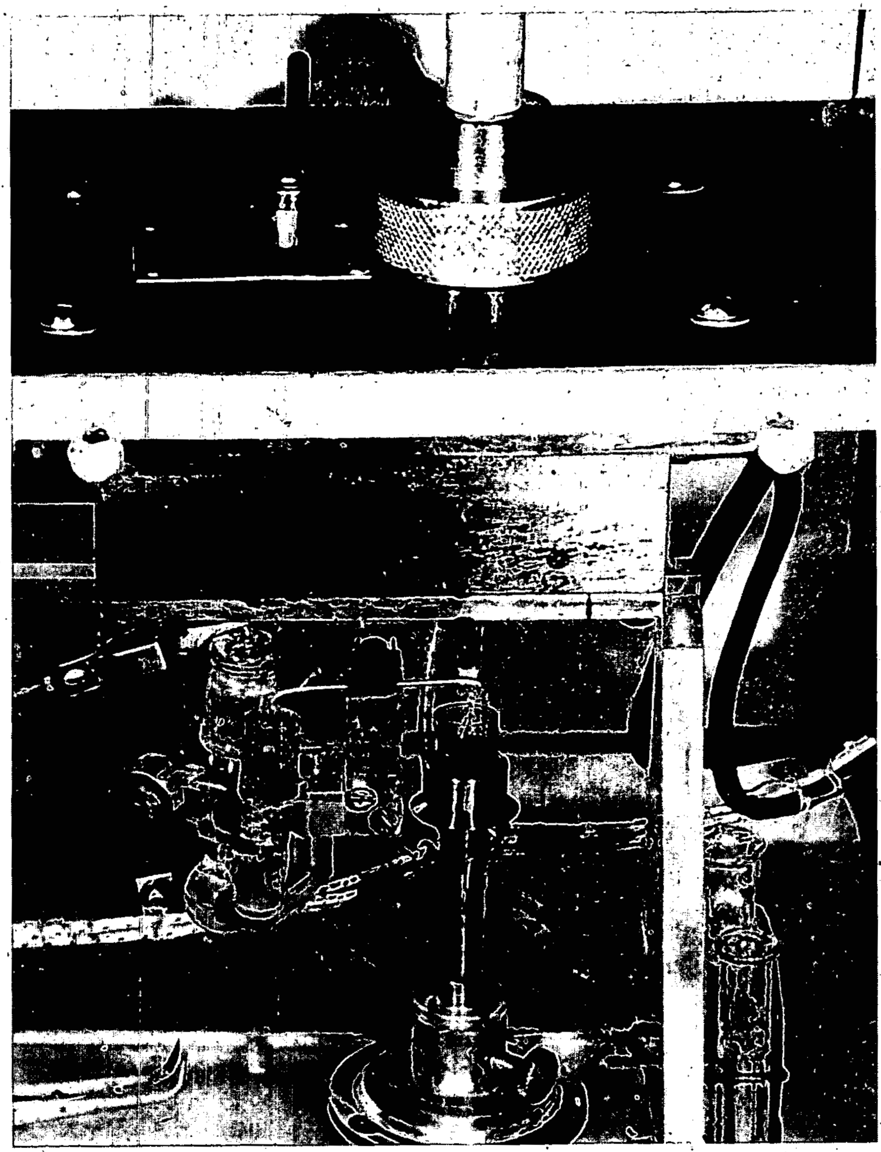


Fig. 7.15 — Microfoil plating apparatus.

scribed in Chap. 9, Sec. 3.1. Both sides of the foil must be counted to measure the total plated activity. The ratio between weight-microgram equivalents and count-microgram equivalents determines the purity percentage of the polonium.

Purity (weight) determinations of this sort have been made on as little as 0.5 per cent of the total solution. The purity of the plated polonium can approach 98 to 100 per cent. A closer examination of these values is somewhat more revealing. If a particular electrode or gauze is plated with 20 curies of polonium which is 98 per cent pure, the weight of the impurities associated with that polonium is less than 100 μg. Furthermore, the total weight of the polonium that would be on the microfoil which was used to determine this purity would be about 22 μg, and the weight of the impurities associated with this polonium would be less than 0.5 μg.

It may be advisable to plate two or more microfoils in order that reliance is not upon only one check of the purity. The polonium on the microfoils can be recovered so that, essentially, no material is lost in the analysis procedure. Microfoils may also serve as a source of small amounts of polonium.

It should be emphasized that the described method of purity determination is indirect in that it does not give the purity of the polonium on the final foils or gauzes; it does indicate the probable purity of this polonium. However, experience has indicated that this method is satisfactory.

11.3 *Neutron Counting.* Light-element impurities may be detected by neutron counting the final plated foil or gauze. Neutrons result from the bombardment of the light-element impurities by the polonium alpha particles, as described in Chap. 12, Sec. 1.4.

Neutron counting may be accomplished by the use of BF_3 or boron-wall neutron-counting tubes in conjunction with a suitable moderator. The two-input neutron mixer described in Chap. 9, Sec. 3.4b has been used for neutron counting of plated foils.

12. CONFINEMENT OF RADIOACTIVITY

The processing of any radioactivity requires the observance of certain rules pertaining to the protection of personnel. Dry-boxing techniques have been widely employed in the processing of polonium. Ventilated hoods similar to those shown in Fig. 13.1 are very useful and adaptable for these processing operations. Chapter 13 discusses the general health physics problems and program at Mound Laboratory; Chap. 13, Sec. 3.1 discusses the problem of confining radioactivity.

Although hoods, such as those shown in Fig. 13.1, were developed for the purpose of confining radioactivity, they just as adequately confine any material which may be used in the processing of the polonium. This confinement is of importance where some of the reagents are highly toxic. It is particularly important to the tellurium process because of the objectionable physiological effects (garlic breath) of tellurium in addition to its toxicity.[72]

13. RECOVERY OF BISMUTH[73]

13.1 *General.* The first bismuth used for irradiation in a reactor had such relatively high silver content that serious health physics problems resulted. One method for obtaining bismuth of lower silver content would be the recovery of irradiated bismuth from which the polonium had been separated. A process has been worked out whereby such bismuth may be recovered for reuse. The purity of the recovered bismuth, with respect to elements other than polonium and silver, can be as good as the purity of virgin bismuth used for irradiation.

The starting material for bismuth recovery is the denitrated solution of bismuth slugs from which the polonium has been removed by the bismuth process (Sec. 8.2), the silver process (Sec. 8.3), or the tellurium process (Sec. 8.4). Either of two general methods might be applicable to the recovery of this bismuth: (1) chemical reduction of the bismuth chloride to metallic bismuth or (2) electrodeposition of the bismuth onto suitable electrodes. After some preliminary studies, electrodeposition was deemed to be the most promising method for recovering bismuth.

13.2 *Electrolysis of Bismuth.* Because of the highly corrosive nature of the hydrochloric acid solution and the chlorine generated during electrolysis, the major problem in the recovery of bismuth would be the selection of the materials for the construction of the bath and the components of the plating cell.

A plating setup such as the one shown in Fig. 7.16 has been used successfully for bismuth plating. The graphite anodes are surrounded by alundum furnace cores to keep the chlorine gas, which is liberated at the anodes, from reacting with the bismuth which is being deposited on the cathodes. Various grades of Owens-Corning Fiberglas also function well as diaphragm material.

A number of metallic cathode materials, such as tantalum, platinum, copper, and bismuth, have been tested. A smooth adherent plate can be obtained on copper, but the copper contaminates the bismuth upon removal of the bismuth. Bismuth cathodes have been used both as the pure metal and as a coating on various backing materials. Cathodes prepared by spraying bismuth onto glass, Vinylite, or ashless filter paper gave satisfactory results. The bismuth plate can be peeled off the glass or Vinylite backing. The ashless filter paper will burn completely during subsequent melting of the bismuth without adding any impurities to the bismuth.

The best quality of plate is obtained when the concentration of bismuth is about 200 g/liter. The maximum current density that can be used is 20 amp/sq ft. Above this current concentration, "treeing" occurs to an excessive degree with the formation of a spongy deposit of bismuth. Under optimum conditions of plating, it is possible to plate out 95 per cent of the bismuth in solution. The average current efficiency for this degree of depletion is 75 per cent.

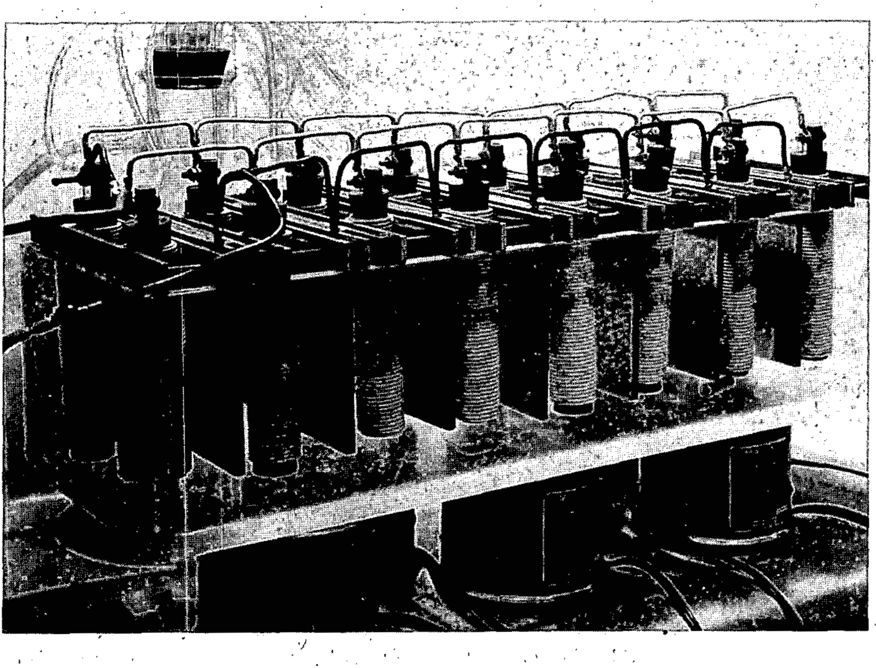


Fig. 7.16—Apparatus for the electrolytic plating of bismuth.

REFERENCES

1. E. M. Larsen and W. C. Fernelius, Possible Sources of Polonium, Report MLM-46-8-65, Oct. 29, 1943 (revised Aug. 15, 1946).
2. J. H. Lum, Requirements of Polonium, Report MLM-M-1489, Dec. 10, 1943.
3. E. Amaldi, O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rosetti, and E. Segrè, Proc. Roy. Soc. London, 149A: 522 (1935).
4. E. E. Rutherford, Phil. Mag., 37: 581-587 (1919).
5. E. E. Rutherford and J. Chadwick, Phil. Mag., 42: 809-825 (1921).
6. E. O. Lawrence and M. S. Livingston, Phys. Rev., 37: 1707 (1931).
7. J. J. Livingood, Phys. Rev., 50: 425 (1936).
8. H. M. Neuman, J. J. Howland, and I. Perlman, Phys. Rev., 77: 720 (1950).

9. H. B. Levy, Isomeric States of Bi^{210}, Report UCRL-2305, August 1953.
10. E. E. Lockett and R. H. Thomas, Nucleonics, 11(3): 14 (1953).
11. J. F. Eichelberger, K. C. Jordan, S. R. Orr, and J. R. Parks, A Calorimetric Determination of the Half Life of Po^{210}, Phys. Rev., 96: 719-721 (1954).
12. M. Goldhaber and R. D. O'Neal, Phys. Rev., 59: 109 (1941).
13. F. C. W. Colmer and D. J. Littler, Proc. Phys. Soc. London, 63A: 1175 (1950).
14. C. Eggler and D. J. Hughes, Quarterly Report (April, May, and June 1950), Report ANL-4476, July 5, 1950, p. 40.
15. S. P. Harris, C. O. Muehlhause, S. Rasmussen, H. P. Schroeder, and G. E. Thomas, Phys. Rev., 80: 342 (1950).
16. H. Palevsky, D. J. Hughes, and C. Eggler, Phys. Rev., 83: 234A (1951).
17. E. Fermi, E. Amaldi, O. D'Agostino, F. Rosetti, and E. Segrè, Proc. Roy. Soc. London, 146A: 483 (1934).
18. S. K. Allison, Letter to C. A. Thomas, Report MLM-44-1-42, Jan. 26, 1944.
19. S. K. Allison, Letter to A. V. Peterson, Report MLM-43-7-11, July 20, 1943.
20. C. A. Thomas, Letter to E. Teller, Report MLM-43-9-4, Sept. 3, 1943.
21. E. Teller, Letter to C. A. Thomas, Report MLM-43-8-19, Aug. 27, 1943.
22. G. Mahfouz and P. M. Cherry, Processing Low-concentration Material, Report MLM-644, Dec. 15, 1951.
23. S. K. Allison, Letter to C. A. Thomas, Report MLM-44-2-14, Feb. 7, 1944.
24. R. E. Meints, C. A. Feichtinger, and A. G. Smith, Progress Report, Report MLM-M-938, Apr. 1-16, 1945.
25. R. D. Evans, Problems of Transportation of Radioactive Substances, Nuclear Science Series, Preliminary Report No. 11, National Research Council, 1951, p. 50.
26. A. G. Smith, R. E. Kneisley, R. E. Meints, and F. R. Stuckey, Progress Report, Report MLM-M-1014, June 16-30, 1945.
27. S. DeBenedetti, Direct Measurement of Polonium Content of Activated Bismuth Slugs, Report MLM-M-1322, June 30, 1944.
28. S. DeBenedetti, E. Larsen, E. Kerver, and J. Payne, Measurement of Polonium by Gamma Rays, Report MLM-M-418, Jan. 21, 1946.
29. S. DeBenedetti, Gamma Rays from Polonium and Measurements of Polonium in Gamma Rays, Report MLM-45-1-57, Jan. 25, 1945.
30. A. Baietti, M. Buford, and W. McLean, Letters to K. Z. Morgan, Report MLM-46-7-71, July 19, 1946.
31. J. H. Payne, Jr., Assay of Slugs, Report MLM-335, July 7, 1949.
32. H. R. Freitag, Memorandum to E. A. Walker, Report MLM-49-6-83, June 16, 1949.
33. M. D. Whitaker, Letter to W. C. Fernelius, Report MLM-45-6-73, June 23, 1945.
34. D. C. Hale, Mechanical Removal of Aluminum Jackets from Bismuth Slugs, Report MLM-485, July 20, 1950.
35. F. J. Leitz, Jr., W. C. Fernelius, and L. B. Silverman, Progress Report, Report MLM-M-1204, Jan. 4-15, 1944.
36. W. C. Fernelius and F. J. Leitz, Jr., Progress Report, Report MLM-M-1250, Mar. 1-15, 1944.
37. R. F. Meehan, Polonium from Irradiated Bismuth, Report MLM-M-772, Mar. 25, 1946.

38. G. D. Nelson, J. H. Payne, Jr., and W. S. Stringham, Jr., The Pilot-plant Stannous Chloride Process, Report MLM-510, Mar. 15, 1950.
39. J. H. Payne, Jr., Progress Report, Report MLM-M-180, June 16–30, 1947.
40. J. J. Burbage and R. E. Meints, Operating Directive for Processing Active Bismuth, Report MLM-45-8-105, Aug. 29, 1945.
41. A. G. Smith, Progress Report, Report MLM-M-1233, Feb. 1–15, 1944.
42. W. C. Fernelius, Progress Report, Report MLM-M-1261, Mar. 16–31, 1944.
43. W. C. Fernelius, Progress Report, Report MLM-M-1272, Apr. 1–15, 1944.
44. F. J. Leitz, Jr., and W. C. Fernelius, Progress Report, Report MLM-M-1281, Apr. 16–30, 1944.
45. F. J. Leitz, Jr., Urea Treatment of Bismuth Solutions Preparatory to Scrubbing, Report MLM-44-6-8, June 2, 1944.
46. J. H. Payne, Jr., The Chemistry of Denitration, Report MLM-47-9-29, Sept. 11, 1947.
47. R. Endebrock, P. Engle, E. McCarthy, and M. Shackelford, Formic Acid as a Denitrating Agent in the Processing of Polonium, Report MLM-47-9-60, Sept. 25, 1947.
48. J. H. Payne, Jr., Progress Report, Report MLM-M-694, Oct. 1–15, 1946.
49. R. K. Harris, Progress Report, Report MLM-M-462, Feb. 16–28, 1946.
50. R. K. Harris, Progress Report, Report MLM-M-478, Mar. 1–15, 1946.
51. M. McEwen and G. Mahfouz, Scrubbing in a Packed Column, Report MLM-46-9-36, Sept. 9, 1946.
52. E. M. Larsen and J. H. Payne, Jr., Progress Report, Report MLM-M-1398, Sept. 1–15, 1944.
53. J. H. Payne, Jr., Progress Report, Report MLM-M-708, Oct. 16–31, 1946.
54. W. Marckwald, Ber., 35: 4239 (1902).
55. W. Marckwald, Ber., 36: 2662 (1903).
56. M. Curie and A. Dieberne, Compt. rend., 150: 387 (1910).
57. M. Guillot, Compt. rend., 190: 1554 (1930).
58. M. Guillot, J. chim. phys., 28: 33 (1931).
59. S. H. Styles and C. L. Rollinson, Pilot-plant Silver Process, Final Report No. 39, Report MLM-M-32, Feb. 13, 1947.
60. W. Marckwald, Ber., 38: 593 (1905).
61. I. Curie, J. chim. phys., 22: 485 (1925).
62. A. Korvezee, J. chim. phys., 30: 132 (1933).
63. L. R. Hafstad, J. Franklin Inst., 221: 202, 209 (1936).
64. E. C. Bratt, Historical Report, Dayton Project, Report MLM-M-286, Oct. 31, 1947, p. 5.11.
65. C. L. Rollinson, Spontaneous Deposition of Polonium on Metals, I, Silver, Seminar Paper, Report MLM-M-774, Apr. 1, 1946, p. 6.
66. "Handbook of Chemistry and Physics," 34th ed., p. 2784, Chemical Rubber Publishing Co., Cleveland, Ohio.
67. C. L. Rollinson and P. M. Hamilton, The Tellurium Process, Report MLM-M-167, Final Report No. 36, June 26, 1947.
68. P. M. Hamilton, C. L. Rollinson, and J. W. Schulte, Progress Report, Report MLM-M-934, Apr. 1–15, 1945.
69. J. W. Schulte, Research on the Electrodeposition of Polonium, Final Report No. 14, Report MLM-M-573, June 20, 1946.

70. R. Wehrmann, The Electrodeposition of Polonium from Hydrofluoric Acid Solutions, Ad Interim Report No. 10, Report MLM-18, Nov. 30, 1947.
71. J. J. Dauby, Mounting Techniques for the Assay of Radioactivity, Report MLM-884, Jan. 20, 1953.
72. P. K. Glass, Toxicity of Tellurium, Report MLM-106, July 25, 1947.
73. W. J. Raiff, P. M. Engle, and M. McEwen, Bismuth Recovery Process, Report MLM-734, Aug. 5, 1952.

Chapter 8

POLONIUM FROM IRRADIATED BISMUTH: STUDIES ON SEPARATION BY DISTILLATION

By P. M. Engle, R. W. Endebrock, and G. C. Cox

1. INTRODUCTION

The separation of polonium from neutron-irradiated bismuth may be effected by direct distillation methods. Some of the advantages of using distillation over chemical methods include a reduction in the requirements for space, manpower, and equipment, the virtual elimination of reagent expense, and a reduction in the amount of radioactive liquid and gaseous wastes. Early experiments at the Dayton Project and at Mound Laboratory were directed toward the development of a feasible method for distilling polonium from irradiated bismuth. Practicable distillation methods for separating polonium from bismuth have been achieved.

Distillation is an established metallurgical process[1–4] that is applicable at both atmospheric pressure and *in vacuo*. Many scientists[5–11] noted that the volatility of polonium could be employed to effect the concentration of polonium from the less volatile materials with which it was found. In 1949 a bismuth-distillation program was initiated at Mound Laboratory.[12] Some of the phases of the Mound Laboratory distillation program included equilibrium studies of polonium-bismuth mixtures, the study of still types and the effect of agitation upon distillation rates, pilot-plant studies, and investigations of the materials of still construction.

2. EQUILIBRIUM STUDIES

By E. F. Joy

The first concern in an investigation of the separation of two materials by distillation is with the degree of separation which can be achieved. If the vapor pressures of the two pure components are known, an estimate of the ease of separation can be made by calculating the relative volatility of the two components. If mixtures of the two give ideal solutions, the calculated relative volatility will give the actual separations which can be achieved in practice. In the case of most solutions the behavior is not ideal. The relative volatility of the two components must then be determined experimentally. After the relative volatilities are determined, they can be used to predict the concentration factor for any size cut or for any desired recovery. The relative volatility is often constant over a wide range of concentrations, and it is a convenient measure of the separation to be expected. The determination of relative volatility is the usual approach in ordinary equilibrant distillation carried out at or near atmospheric pressure. However, to attain appreciable distillation rates and satisfactory separation factors, vacuum distillation is necessary with polonium-bismuth mixtures.

The conditions during high-vacuum distillation are quite different from ordinary equilibrant distillation. At low pressure there is no appreciable interchange of molecules between the vapor and liquid. Evaporation takes place at the liquid surface, but condensation of vapor on the liquid is negligible. The evaporation rate is governed by Langmuir's equation[13] which relates the rate of evaporation of a pure metal in vacuum to its vapor pressure. Langmuir's equation was applied to the binary bismuth-polonium solution making appropriate assumptions regarding the partial pressure as a function of concentration for each metal. The equations for the two metals were combined and integrated to give an isothermal equation which is identical with the Rayleigh equation[14] usually applied to simple batch equilibrant distillation. As applied to the distillation of polonium from bismuth,

$$\log \frac{Po_2}{Po_1} = \alpha \log \frac{Bi_2}{Bi_1} \tag{8.1}$$

where α = the relative volatility and is $\gamma_{Po} P_{Po} / P_{Bi}$
Po_1 = the amount of polonium in the original mixture
Po_2 = the amount of polonium in the residual liquid
Bi_1 = the amount of bismuth in the original mixture
Bi_2 = the amount of bismuth in the residual liquid
γ_{Po} = the activity coefficient of polonium in the dilute solution
P_{Po} and P_{Bi} = the vapor pressures of pure polonium and bismuth, respectively

Alternatively, this can be expressed in terms of Y, the fraction of the original polonium distilled, and X, the fraction of the original bismuth distilled:

$$\log (1 - Y) = \alpha \log (1 - X) \tag{8.2}$$

from which the concentration factor Y/X is found to be

$$\frac{Y}{X} = \frac{1 - (1 - X)^{\alpha}}{X} \tag{8.3}$$

The experimental data on the distillation of polonium from dilute solution in bismuth have been found to fit these relations. The relative volatility was found to be constant over at least a 10,000-fold range of concentrations. The value found was less than that calculated from the vapor pressure of the pure metals, indicating negative deviation from Raoult's law (γ_{Po} less than 1).[15] Polonium does follow Henry's law,[16] as shown by the constancy of the relative volatility. This would be expected for the minor component in the dilute-solution range.

The effect of temperature on the relative volatility was investigated over the range of 450 to 850°C. The effect of change of orifice size from essentially unrestricted distillation down to the Knudsen condition[17] for effusion (orifice diameter less than $1/_{10}$ the mean free path) was followed. Equilibrium conditions giving a maximum volatility were achieved over a wide range of orifice sizes. The rates of distillation of bismuth for both the Langmuir and Knudsen conditions were used to calculate the vapor pressure of bismuth. The close agreement of the vapor pressure with the literature values in the range in which it has been previously measured is evidence for the validity of the experimental approach used.

Irradiated slug bismuth was given a preliminary treatment to obtain reproducible samples for the distillation studies. Samples of irradiated bismuth (3 to 4 g) were melted in vacuum to degas the metal and were then filtered through a 1.5-mm bore capillary to remove the surface oxide. The polonium content was determined by dissolving a representative sample in nitric acid and making an alpha-particle assay. The starting concentration was about 10^{-6}M in polonium.

Distillations were made in the apparatus shown in Fig. 8.1. The fraction of the original bismuth distilled and the fraction of the original polonium distilled, X and Y, respectively, were determined by difference for each successive distillation.[18] These values were used in Eq. 8.3 to calculate the relative volatility.

The constancy of the relative volatility α at various size cuts for distillations at 500°C is shown in Table 8.1. These cover a 10,000-fold range in the starting concentration of polonium and show clearly that there is no trend in relative volatility as the distillation progresses. An average α of 199.3 was obtained.

Similar results were obtained for open-cup distillations at other temperatures in the range of 450 to 700°C. To obtain measurements at higher temperatures (550 to 850°C), distillations were made from a quartz cup having a restricting orifice. The orifice reduced the rate of distillation so that measurements could be made without having to use excessively short distillation times. The results of the two sets of experiments are given in Table 8.2. The data show a regular trend of decreasing relative volatility with higher temperatures. This would be expected because the vapor pressure of polonium does not increase as rapidly with increase of temperature as does that of bismuth. The restricted-orifice distillations gave higher relative volatilities than the open-cup distillations for the same temperature. It is believed that the effect of surface depletion of polonium by too rapid evaporation should be eliminated in the restricted-orifice experiments and that more

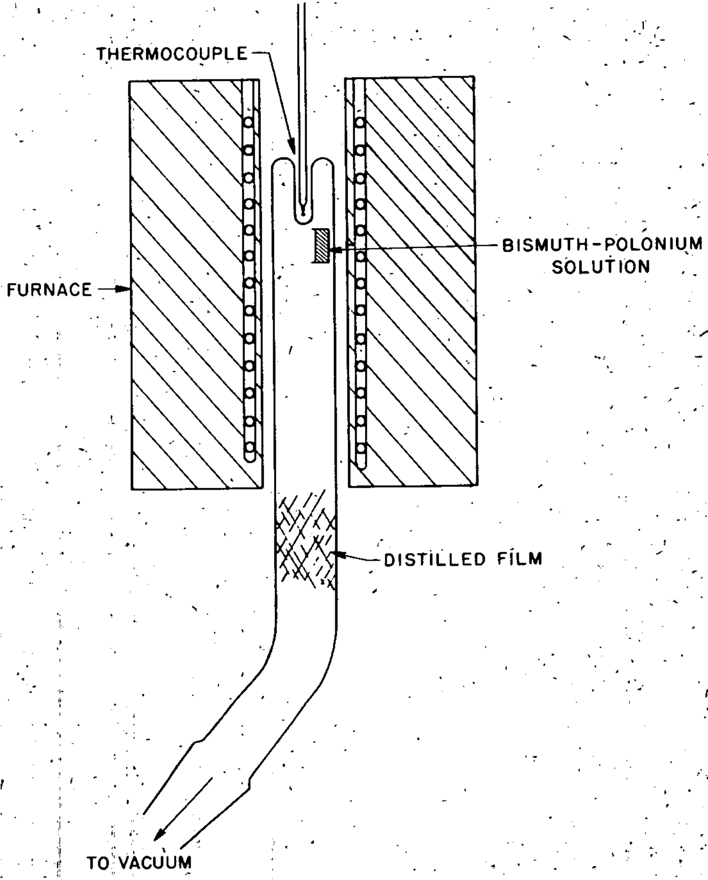


Fig. 8.1—Equilibrium distillation apparatus.

nearly equilibrium conditions are reached. The unrestricted distillations show the relative volatilities which can be obtained at maximum distillation rates.

Table 8.1 — Variation of Relative Volatility with Size of Cut, Unrestricted Distillation at 500°C

Experiment No.	Bi distilled, %	Po distilled, %	Relative volatility α
1	0.335	47.81	193.7
2	0.549	64.86	189.6
3	0.968	85.47	198.7
4	1.45	94.34	196.8
5	1.508	95.51	204.2
6	2.18	98.79	200.2
7	2.935	99.79	207.1
8	4.509	99.99	199.6
9	5.624	99.99	203.5
		Average	199.3

Table 8.2 — Variation of Relative Volatility with Temperature

Unrestricted distillation		Restricted-orifice distillation	
Temp., °C	Relative volatility α†	Temp., °C	Relative volatility α†
450	282.3	550	172.8
500	199.3	650	96.5
600	105.2	700	73.5
700	58.2	750	57.7
		850	34.6

† The values of α are averages of several experiments at each temperature.

The effect of changing orifice size on relative volatility is shown in Table 8.3. The relative volatility is essentially constant over a wide range of orifice sizes, again indicating that equilibrium conditions are obtained in the restricted-orifice measurements.

The rates of distillation of bismuth were used to calculate the vapor pressure of bismuth. Initial experiments with pure bismuth gave results identical to those with slug bismuth containing polonium at 10^{-6}M concentration. Rates from all the distillation data were therefore used in calculating the vapor pressure of bismuth. An equation based on a least-squares reduction of the data is given in Eq. 8.7. The open-cup (Langmuir) and restricted-orifice (Knudsen) experiments gave no significant difference in the calculated vapor pressure, indicating that the accommodation coefficient for bismuth is close to 1. The vapor pressures obtained agree well with the literature values at the higher temperatures (above 600°C) and extend the range downward to 450°C where reliable measurements have not been made previously.

The partial pressure of polonium in 10^{-6}M to 10^{-10}M solution in bismuth was calculated from the instantaneous rate of distillation of polonium obtained in the Knudsen effusion experiments and was found to follow Henry's law in these dilute solutions. The volatility of polonium, i.e., the partial pressure divided by the mole fraction of polonium, was calculated and was found to be much less than the vapor pressure of pure polonium found experimentally by Brooks.[19] The deviation of polonium from ideal behavior in these dilute solutions was expressed as the activity coefficient,

Table 8.3 — Effect of Orifice Area on Relative Volatility at a Temperature of 650°C

Orifice area, sq mm	Area ratio†	Relative volatility, α‡
0.1512	0.00127	97.5
0.3394	0.00284	96.6
0.915	0.00768	95.7
2.25	0.0189	97.0
5.57	0.0467	96.7

† Area ratio is the ratio of the area of the orifice to the area of the distilling surface which is 119.2 sq mm.

‡ The values of α are averages of duplicate experiments.

$$\gamma = \frac{\text{volatility of Po}}{\text{vapor pressure of pure Po}} \tag{8.4}$$

Equations expressing the volatility, the vapor pressure of polonium, and the activity coefficient of polonium as a function of temperature are given below.

The vapor-liquid equilibrium of dilute solutions of polonium in liquid-bismuth metal has been investigated over the temperature range of 450 to 850°C. Variables which have been investigated are change of concentration, change of temperature, and effect of orifice size. The relative volatility of polonium and bismuth has been determined as a function of temperature and is independent of concentration over the range studied. The equations obtained for the relative volatility α are, for unrestricted distillation (maximum distillation rate),

$$\log \alpha = -4.9828 + \frac{18{,}220}{(t + 2001)} \qquad (8.5)$$

and, for restricted-orifice distillation (maximum enrichment),

$$\log \alpha = -3.0073 + \frac{10{,}350}{(t + 1423)} \qquad (8.6)$$

where t is the temperature in degrees centigrade.

The bismuth vapor pressure P_{Bi}, in millimeters of mercury, is given by

$$\log P_{Bi} = -\frac{10{,}051}{T} + 8.4621 \qquad (8.7)$$

where T is the temperature in degrees Kelvin. From the slope of this curve the heat of vaporization of bismuth was calculated as 46.0 kcal/mole.

The distillation rate w of bismuth, in grams of bismuth per square centimeter per second, is given by

$$\log w = 8.3878 - \frac{10{,}051}{T} - \frac{1}{2}\log T \qquad (8.8)$$

where T is the temperature in degrees Kelvin.

The pure-polonium vapor pressure P_{Po} (as determined by Brooks[19]), in millimeters of mercury, is given by

$$\log P_{Po} = -\frac{5377.8}{T} + 7.2345 \qquad (8.9)$$

where T is the temperature in degrees Kelvin.

The volatility V of polonium from dilute solution in bismuth, in millimeters of mercury, is given by

$$\log V = -\frac{8106}{T} + 8.3521 \qquad (8.10)$$

where T is the temperature in degrees Kelvin.

The activity coefficient γ of polonium in dilute bismuth solution is given by

$$\log \gamma = -\frac{2728.3}{T} + 1.1176 \qquad (8.11)$$

where T is the temperature in degrees Kelvin.

From the slope of the curve of log γ as a function of T, the partial molal heat of solution $\bar{L}$ of polonium in excess bismuth is $\bar{L} = -12.6$ kcal/mole.

3. PRELIMINARY DISTILLATION STUDIES

3.1 *Experimental Stills.* The first distillation experiments at Mound Laboratory were qualitative tests in which platinum foils, upon which polonium had been plated, and metallic bismuth were placed side by side in a small cylindrical nickel tube open at one end.[12] A cool Pyrex-glass cartridge extended over the open end of the tube to collect the vaporized material, and the tube and cartridge were enclosed in a glass vacuum system. Slight mirrors appeared on the cooled glass cartridge upon heating the nickel tube to a dull red heat. Heating was by induction and was carried out at various residual helium pressures. These mirrors produced good scintillations on zinc sulfide paper, indicating that polonium had been transferred.

Five quantitative experiments employing this method of distillation were completed, utilizing the equipment shown in Fig. 8.2. Each experiment was run as a series of cycles,[12] and the results of these cycles showed that (1) polonium could not be distilled in the presence of aluminum, (2) some bismuth distilled with the polonium, and (3) very little polonium was retained in the melt after the last cycle was completed.

In an attempt to improve upon the Pyrex-glass still, a low-carbon-steel fractionating still was constructed with a column that was twice as high as the still-pot diameter. One complete run of four cycles totaling 15½ hr was made, and the data accumulated indicated a high polonium-to-bismuth concentration factor but a rather low rate of polonium recovery for this type of still.

The stripping apparatus shown in Fig. 8.3 was constructed[20] in order to demonstrate that irradiated bismuth could be depleted of its polonium content at a rapid rate by distillation. The irradiated bismuth charge was placed in the annulus formed between the steel outer wall and the central tube. The steel assembly was loosely capped and placed in the quartz housing. The quartz housing was evacuated, and the upper 4 in. of the steel stripper was heated by an induction heater to about 1000°C. Vaporized bismuth and polonium passed up through the annulus and down through the central tube to be collected in a small collector tube (not shown) in the cooled bottom of the quartz housing. After each heating cycle, the collector was removed and the collected product analyzed for both polonium and bismuth. It was demonstrated that, under sufficiently severe temperature conditions, bismuth can be depleted of its polonium content quite rapidly by distillation. The high temperature and lack of any fractionation or partial condensation ef-

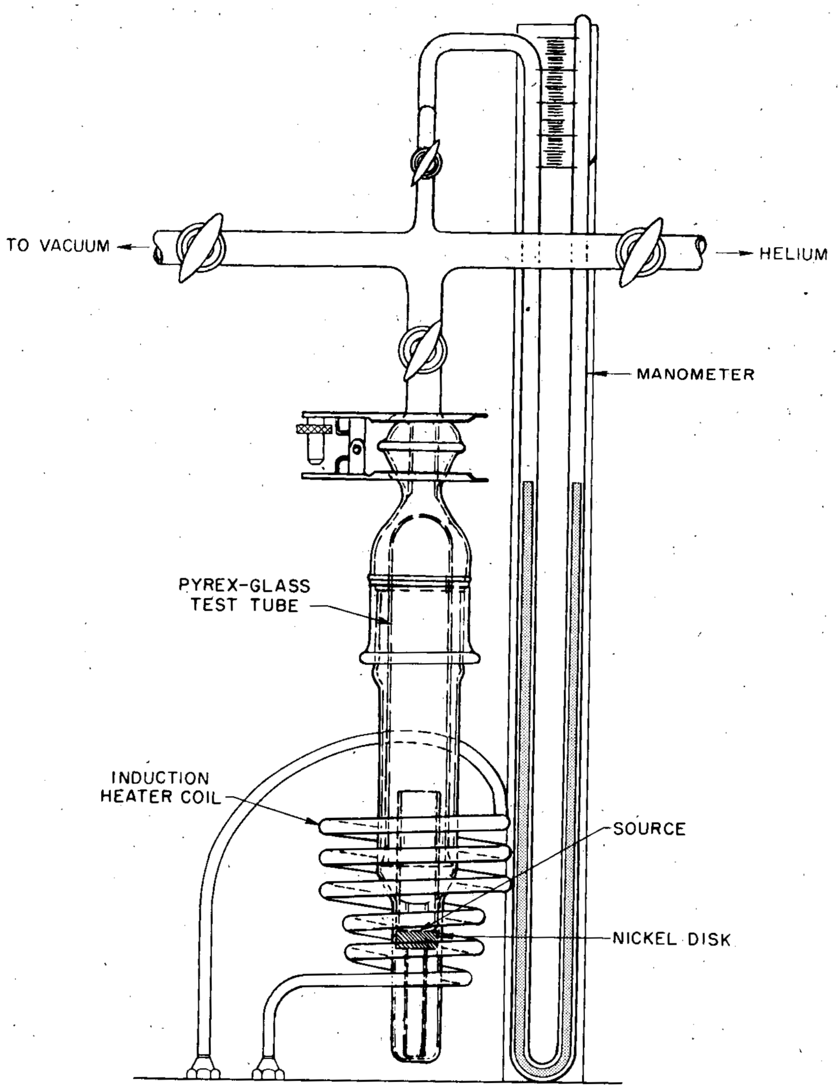


Fig. 8.2—Experimental Pyrex-glass still.

fect resulted in large amounts of bismuth in the collected products; hence low concentration factors resulted.

The rates of depletion for the various stills used in the early experiments at Mound Laboratory are compared in Figs. 8.4 and 8.5. These figures show the variation in the concentration factor with degree of product collection for these experiments.

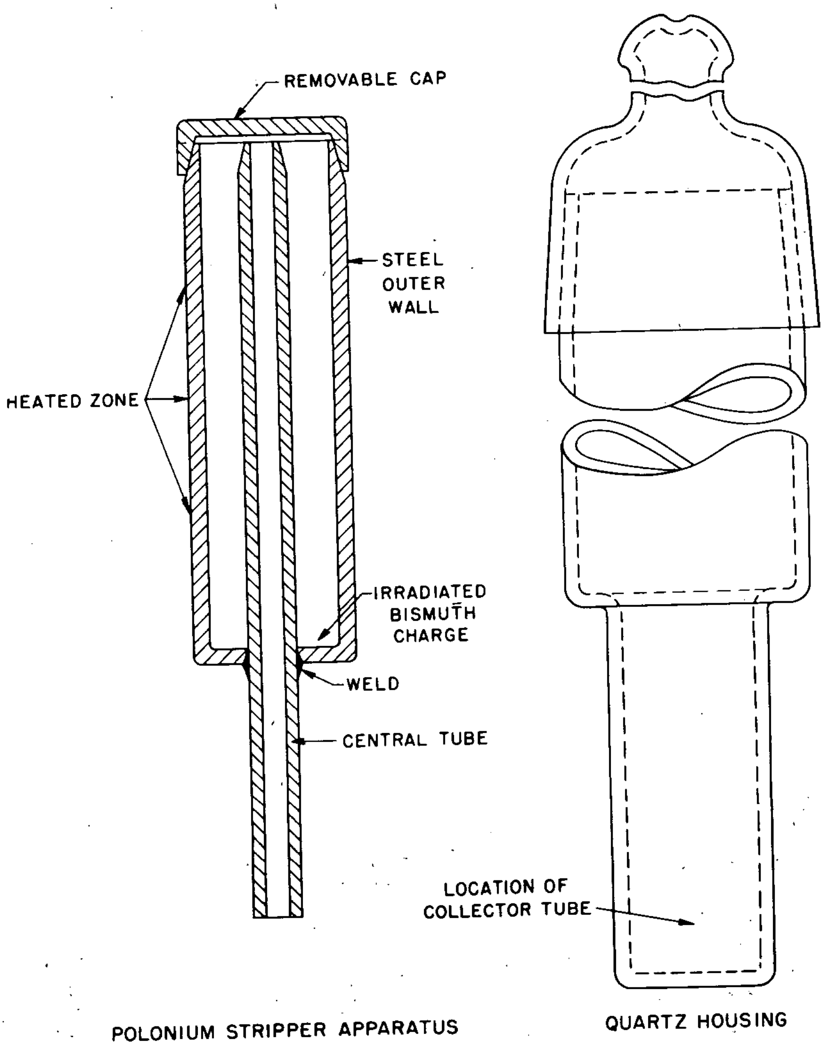


Fig. 8.3 — Polonium stripping apparatus.

3.2 *Agitation.* During some of the early work on the distillation of polonium from irradiated bismuth, it appeared that small quantities of a gas or gases were liberated during the distillation. The effect of the liberation of gas during distillation was studied and, being apparently beneficial, was eventually incorporated into the design of distillation units with sparging inlets.

The rate at which polonium is volatilized from the surface of the bismuth melt is rapid at high temperatures; hence the rate of diffusion of the polonium from the body of the melt to the surface is assumed to be

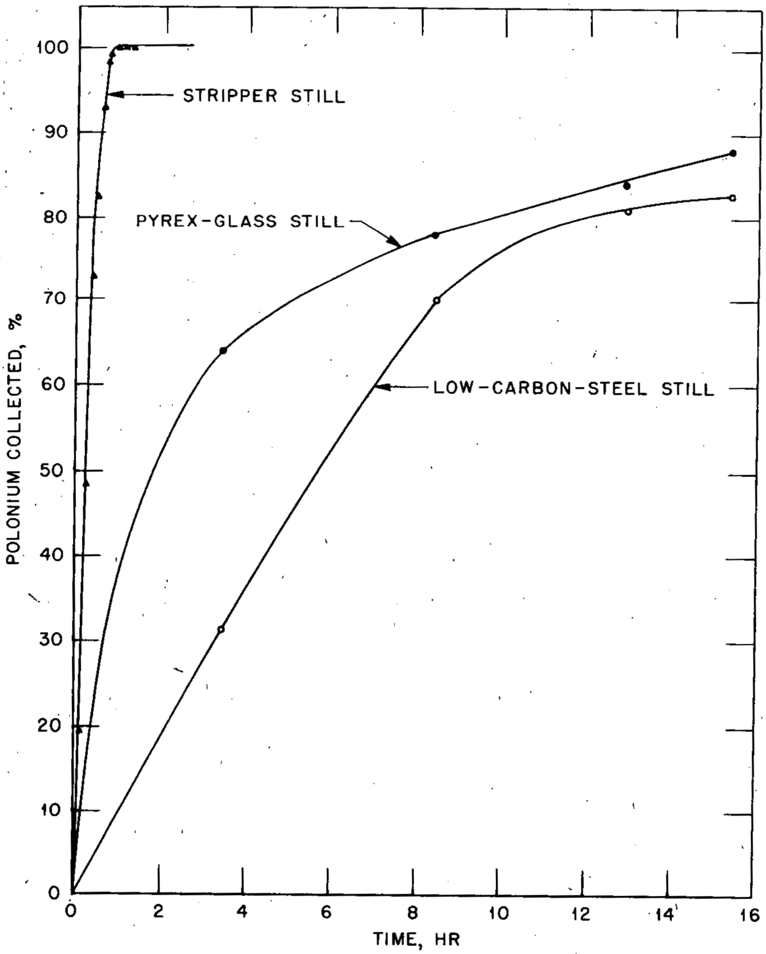


Fig. 8.4 — Polonium collection rates in experimental stills.

the rate-controlling mechanism. Experiments which involved agitating the melt confirmed this assumption, at least to a degree. Several methods of ordinary mechanical agitation were investigated briefly; but, owing to the temperature and vacuum requirements, the difficulties experienced proved this method to be impractical.

Two test units were constructed to investigate the effect, on distillation,[21] of nonmechanical agitation of the bismuth. One of the stills used was a cylindrical unit divided into four compartments, each compartment being equipped with a separate, identical, product collection tube. After the first compartment was loaded and the irradiated bismuth was melted, this compartment acted as a control which allowed distillation with agitation. By manipulating the pressures in each compartment, the bismuth was sprayed in turn into each successive compartment where further distillations occurred. This test indicated an average distillation rate 15 times greater with agitation than without agitation.

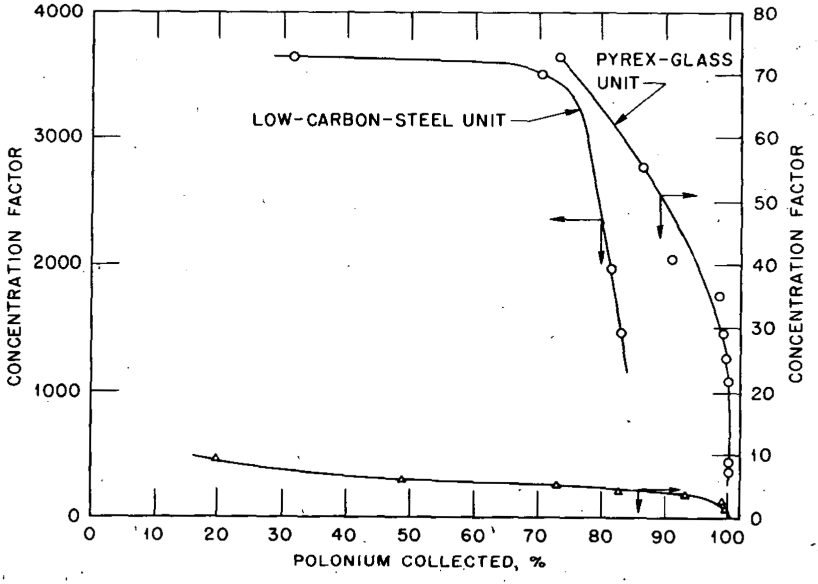


Fig. 8.5 — Concentration factor vs. per cent polonium collected in experimental stills.

The second still that was used was constructed from a Pyrex cylinder that had a fritted Pyrex disk sealed in the bottom. Helium was passed through the disk and into the molten bismuth, and the pressure above the bismuth was adjusted to permit sufficient gas leakage into the bismuth to give a gentle agitation. The bismuth was heated by an induction heater. Based on the depletion of polonium from the bismuth melt rather than on product recovery, this test showed that, of the original 1.480 curies of polonium in the charge, 71.8 per cent, or 1.062 curies, was distilled from the melt. The polonium transfer occurred during a 60-min distillation period, and the average polonium transfer rate was 17 mc/min. In the second test employing a fritted Pyrex disk, the rate of polonium recovery was four times faster when gas agitation was employed as compared to a test wherein no gas agitation was employed.[22]

4. PILOT-PLANT STUDIES

Three fractionating distillation units were constructed (Fig. 8.6) which incorporated inlets for helium sparging of the melt. One unit was constructed of low-carbon steel, the next unit was constructed of transformer steel (3 per cent silicon), and the third unit was similar to the first except for the depth of the still pot. These units were successfully operated for several hundred hours each.

The experimental arrangement of the low-carbon-steel still consisted of defining the middle of the fractionating column and the middle of the still pot as the points where temperature control would be maintained. Under these conditions of operation it appeared that the column temperature controlled the purity of the collected product while the still-pot temperature controlled the rate at which polonium was distilled from the bismuth. In these experiments 3-hr distilling cycles were used.

The relation between column temperature and the amount of both polonium and bismuth collected with the still bottom held constant at the experimentally determined optimum temperature is shown in Fig. 8.7. The polonium-recovery curves are approximately exponential, and the bismuth-collection curves are linear. Readjustments in the column temperature setting (with the still bottom maintained at optimum temperature) will permit an operating point to be found where the product concentration is improved; however, this improvement is attained at the expense of longer distillation times.

Spattering of bismuth into the still column was minimized by inserting a baffle into the bottom of the column. Although this baffle constricted the column to less than $\frac{1}{8}$ of its cross-sectional area, distillation rates and polonium-recovery yields appeared to be unaffected.

A series of distillation experiments was run without sparging, and inexplicably the data indicated that the lack of sparging had little effect upon the rate at which polonium was distilled from the melt.

A duplicate of the low-carbon-steel sparging still was constructed from transformer steel because corrosion studies (Sec. 5) indicated that transformer steel was corroded to a lesser degree by molten bismuth than was low-carbon steel. The data obtained from experiments performed in these units showed that:

1. Higher product concentrations are obtained from the transformer-steel sparging still, but lower product recoveries are found.

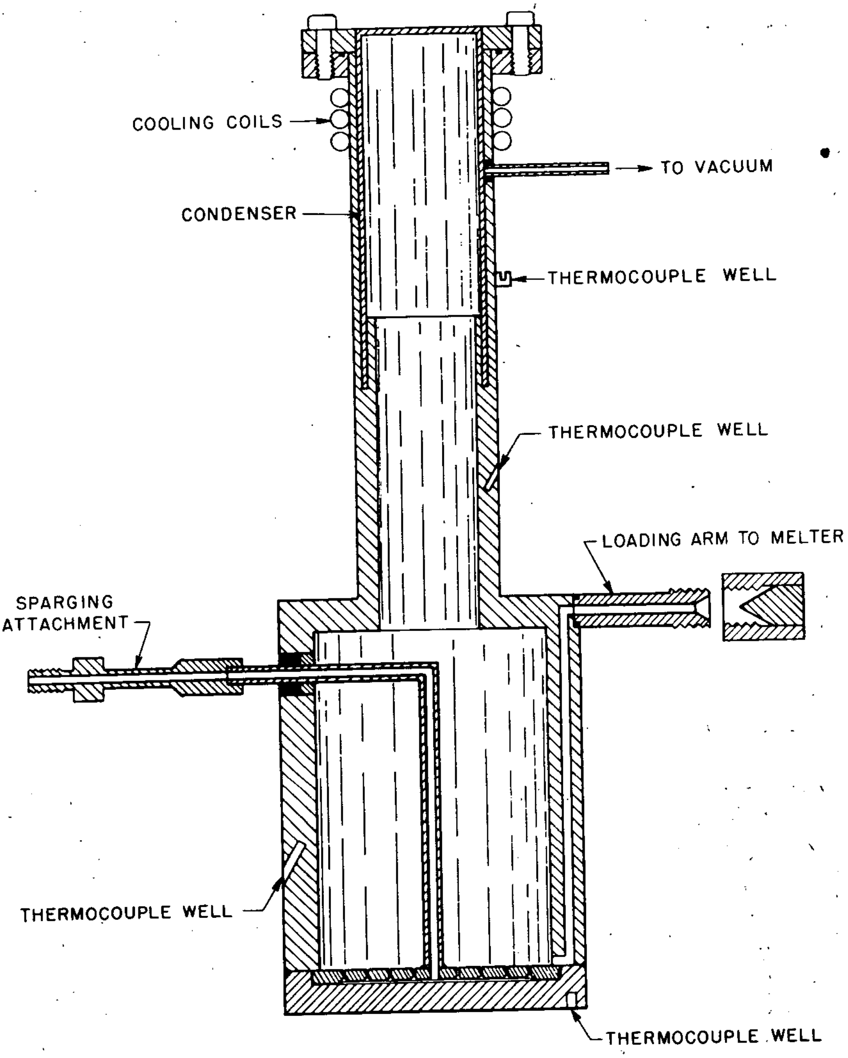


Fig. 8.6 — Fractionating distillation still.

2. Higher distillation-unit wall temperatures are required in the transformer-steel still for comparable distillation rates.
3. Approximately 10 times more polonium reacted with and was retained by the transformer steel than with the low-carbon steel.

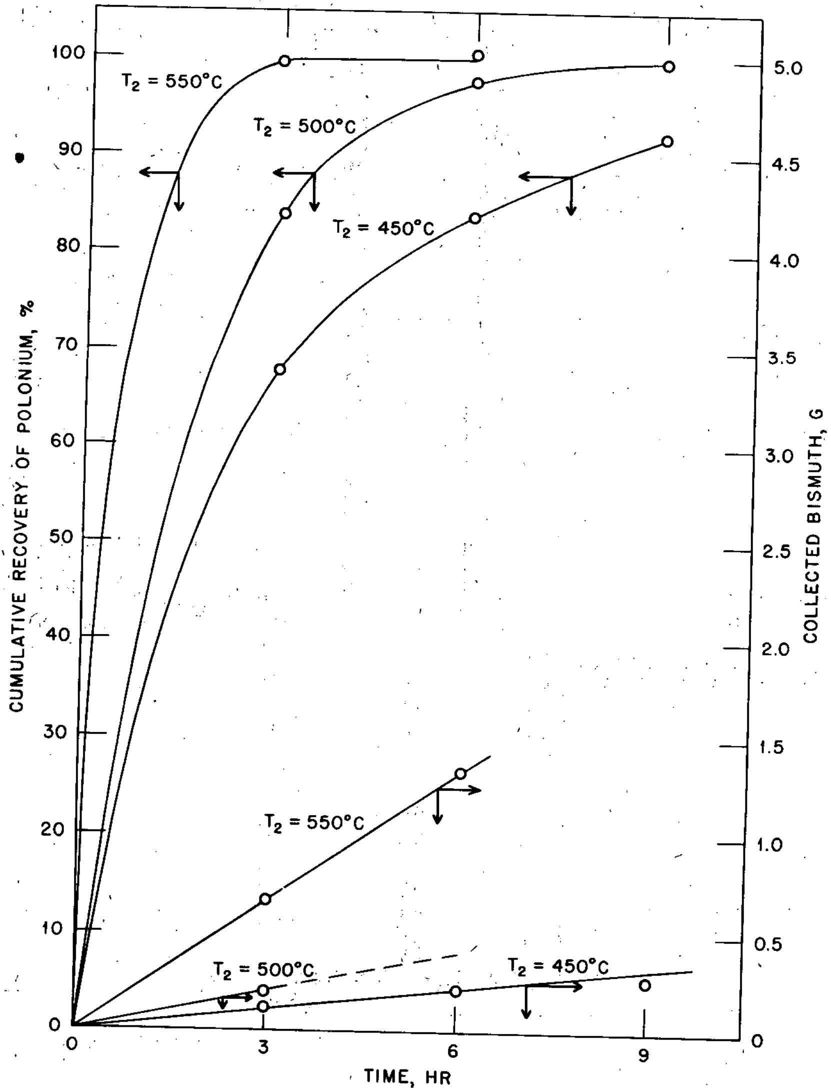


Fig. 8.7—Recovery of polonium from low-carbon-steel fractionating still as a function of column temperature.

The effects on the distillation of polonium from the bismuth melt, as a function of the depth of the melt, were investigated with a low-carbon-steel deep-well still. The height of the still bottom, and consequently the distance between the melt (with equivalent amounts of bismuth) and the collector, was increased by a factor of 3 over the first low-carbon-steel pilot-plant still.

Still-bottom temperatures of 750 and 850°C, center-column temperatures of 650 and 760°C, and top-column temperatures of 275 and 375°C were selected as experiment variables, in addition to the increased depth of melt, because previous experience had indicated that these temperatures would provide approximately optimum distillation of polonium from the molten bismuth.

The results obtained using this still under the established temperature conditions showed that:

1. The per cent depletion (total amount of polonium leaving the melt vs. total amount of polonium remaining in the melt) is dependent almost entirely on the still-bottom temperature. However, with either 850 or 750°C as the still-bottom temperature, only a few hours was necessary to deplete the melt essentially to 100 per cent.
2. The per cent yield (total amount of polonium collected vs. total amount of polonium leaving the melt) was dependent almost entirely on the top-column temperature. Only a few hours was required to obtain 100 per cent yields with either top temperature used.
3. The concentration factor (ratio of polonium to bismuth collected vs. polonium to bismuth originally in the melt) was dependent almost entirely on the top temperature. With this temperature at 275°C, concentration factors as high as 55,000 were attained.
4. The center-column temperature had no noticeable effect on the results.
5. The depth of melt had no noticeable effect on results.
6. Helium sparging of the melt produced no significant difference in results.

A purification still (Fig. 8.8) was constructed to supplement the deep-well still so that the number of distillation steps for obtaining over 90 per cent pure polonium could be determined. In this still the collector from the deep-well still was inverted and inserted into the purification still so that it acted like a still bottom. The material from this piece was then distilled to another similar collector located at the top of the purification still in the cold zone. In this setup successive distillations could be achieved. It was determined that only one additional distillation was necessary to obtain over 90 per cent pure polonium when collectors from the deep-well still were used as feed.

5. MATERIALS OF STILL CONSTRUCTION

The corrosion of metals and other materials by molten bismuth has been reported.[23–27] A number of materials were tested for corrosion

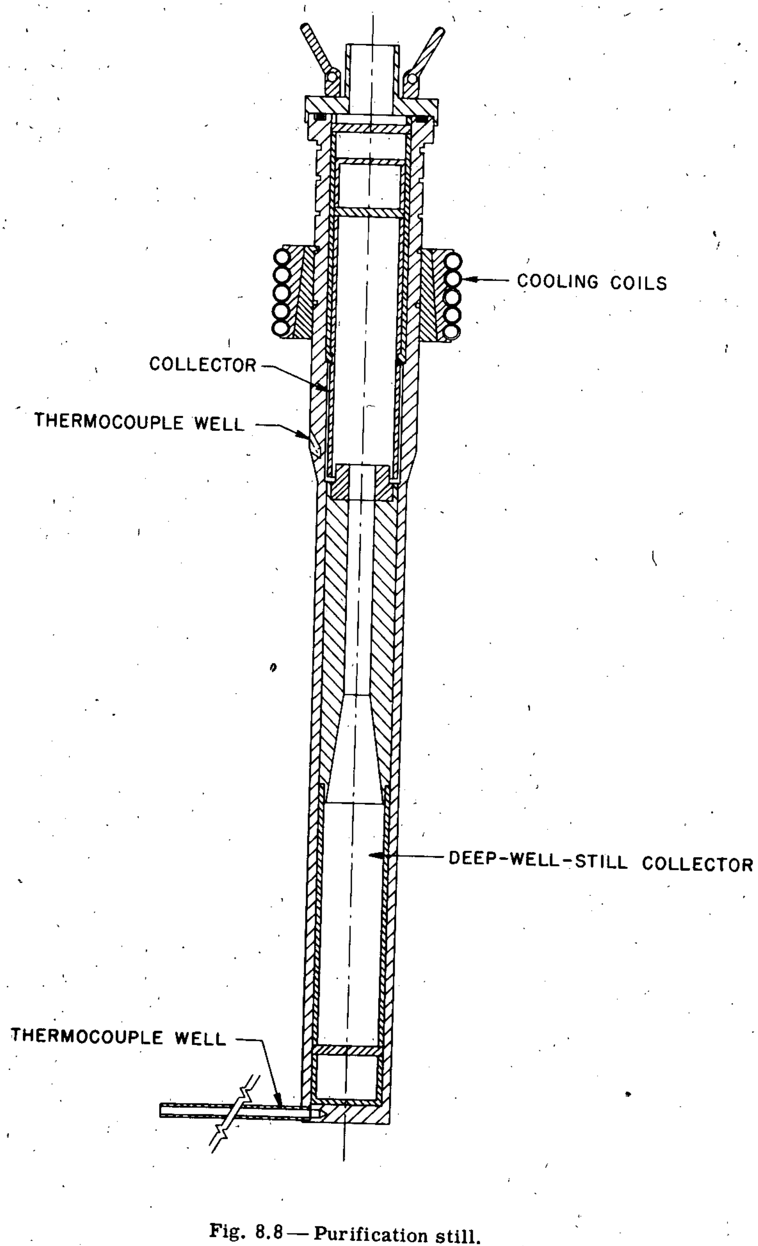


Fig. 8.8 — Purification still.

by bismuth, under specified conditions, to determine their applicability in the Mound Laboratory distillation program. These investigations[27] covered the static corrosion of many materials by liquid bismuth at 750 and 850°C. The materials investigated included low-alloy steels, silicon steels, stainless steels, and heat-resistant superalloys. The metals were examined visually and metallographically after exposure to the bismuth, and the bismuth was analyzed for impurities absorbed from these metals. In fairly long-term tests, Armco iron, low-carbon steels, and chromium-plated samples were found to be severely attacked by the bismuth; and the chromium alloys, stainless steels, and superalloys were moderately attacked by the bismuth. A 2.9 per cent silicon transformer steel and Duriron were the only materials tested which exhibited good corrosion resistance to bismuth at 750 and 850°C.

Table 8.4 — *Corrosion of Low-carbon Steel by Molten Bismuth*

Test No.	Bismuth charge, g	Temp., °C	Vacuum, mm Hg	Duration of test, hr	Bismuth recovered, g	Iron in bismuth, %	Iron in condensation ring, %
1	100	980	1	24	81	0.005	
2	100	980	1	24	93	0.005	28
3	100	850	1	48	73.7	0.006	
4	100	850	1	48	78.0	0.003	15.5
5	100	850	1	78	78.0	0.05	
6	100	850	1	78	Tube failed when weld opened		30
7	100	850	0.7	100	80.0	0.2	
8	100	850	0.7	100	85.8	0.24	26†
9‡	100	850	0.7	100	97	0.08	0.04

†Weight of condensation ring, 17.5 g.
‡In quartz tube, with piece of steel having area of 3.34 sq cm.

Over a period of time several other series of corrosion tests of various materials by bismuth have been made at Mound Laboratory. Denver Hale reported some early corrosion experiments.[27] Table 8.4 lists his data for the corrosion of low-carbon steel by bismuth. The first eight tests were performed by refluxing bismuth in a steel cylinder in a residual nitrogen atmosphere of about 1 mm Hg pressure. A condensation ring containing a brittle deposit was found (in all cases) on the tube wall just above the heated zone. Although this deposit appeared to be a bismuth alloy, heating a portion to 1000°C caused bismuth to flow out of the ring, leaving a residue of the same form as the original ring. This residue appeared to be a spongy deposit of condensed iron containing absorbed bismuth.

Tests on miscellaneous metals were performed by exposing the metal samples to bismuth which was contained in a quartz tube.[21,28,29] Duriron was more resistant to bismuth than any other material tried. This work was the first indication that silicon had a beneficial effect on the corrosion resistance of iron alloys to bismuth. Additional data were obtained on the corrosion resistance of high-temperature alloys. These tests indicated that high-temperature alloys (for example, alloy numbers S-590 and 19-9DL) have fairly good corrosion resistance to melted bismuth.

Little information is available on the combination of polonium with the materials of still construction. Investigations by Goode[30] indicated that polonium forms compounds with zinc, lead, platinum, nickel, silver, and sodium; compounds with gold, tantalum, iron, and aluminum were not found. A test[28] performed to simulate still conditions consisted of sealing 1 curie of polonium in a small steel container and repeatedly heating and cooling it. After a number of heating and cooling cycles, the container was opened and heated to a high temperature to drive off the free polonium. The container retained 2.6 per cent of the original polonium. A second test showed that only 0.007 per cent of the polonium was retained.

6. CONCLUSIONS

Effective methods for the separation of polonium from irradiated bismuth by distillation have been achieved. Equilibrium studies of this method of separation have indicated that this type of purification procedure should be practicable, and pilot-plant studies have resulted in the development of suitable distillation equipment for the performance of the separation. The feasibility of using distillation methods on a plant-scale basis has not been investigated.

REFERENCES

1. W. T. Isbell, Metals Technol., 14: No. 3, Tech. Pub. No. 2138 (1947).
2. W. T. Isbell, U. S. Patent No. 2,422,967, June 24, 1947.
3. W. T. Isbell, U. S. Patent No. 2,461,280, Feb. 8, 1949.
4. P. M. Ginder, W. M. Pierce, and R. K. Waring, U. S. Patent No. 1,994,349, Mar. 12, 1935.
5. F. Paneth and G. Hevesy, Monatsh., 34: 1605-1608 (1914).
6. E. Rona and E. A. W. Schmidt, Z. Physik, 48: 784-789 (1928).
7. P. Bonet-Maury, Ann. phys., 11: 253-341 (1929).
8. E. Rona, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa, 141: 533-537 (1932).
9. K. Schwarz, Z. physik. Chem., A168: 241-247 (1934).
10. H. Jedrzejowski, Acta Phys. Polon., 2: 137-142 (1933).
11. M. Hoffer, Sitzber. Akad. Wiss. Wien, Math. naturw. Kl., Abt. IIa, 144: 393-396 (1935).
12. R. W. Endebrock, J. E. Bersuder, R. T. Bucsko, and R. L. Bates, Status of Metal Distillation Problem, Report MLM-376, Aug. 8, 1949.
13. I. Langmuir, Phys. Rev., 2: 329 (1913).

14. J. H. Perry, editor, "Chemical Engineers Handbook," 2d ed., p. 1382, McGraw-Hill Book Company, Inc., New York, 1941.
15. J. H. Perry, editor, "Chemical Engineers Handbook," 2d ed., pp. 675, 1353, McGraw-Hill Book Company, Inc., New York, 1941.
16. J. H. Perry, editor, "Chemical Engineers Handbook," 2d ed., pp. 675, 1355, McGraw-Hill Book Company, Inc., New York, 1941.
17. M. Knudsen, "The Kinetic Theory of Gases," Methuen & Co., Ltd., London, 1934.
18. E. F. Joy, Quarterly Progress Report, Report MLM-866, p. 16, June 30, 1953.
19. L. Brooks, The Vapor Pressure of Polonium, Information Meeting Paper No. 9, Report MLM-189, Sept. 13, 1948.
20. R. W. Endebrock, R. N. Augustson, R. T. Bucsko, and David C. Hale, Quarterly Progress Report, Report MLM-570, pp. 27-35, June 18, 1951.
21. R. N. Augustson, R. W. Endebrock, P. M. Engle, H. B. Honius, H. J. Morris, and H. L. Rawlings, Quarterly Progress Report, Report MLM-602, pp. 32-39, Aug. 6, 1951.
22. R. N. Augustson, R. W. Endebrock, and H. L. Rawlings, Quarterly Progress Report, Report MLM-623, pp. 32-41, Nov. 19, 1951.
23. R. N. Lyon, editor, "Liquid-metals Handbook," 2d ed., NAVEXOS-P-733 (Rev.), pp. 173-176, Office of Naval Research, June 1952.
24. T. A. Coultas, Corrosion of Refractories by Tin and Bismuth, Report NAA-SR-192, Sept. 15, 1952.
25. W. J. Hallett and T. A. Coultas, Dynamic Corrosion of Graphite by Liquid Bismuth, Report NAA-SR-188, Sept. 22, 1952.
26. H. A. Pray, R. S. Peoples, and W. K. Boyd, Corrosion by Molten Bismuth, Report BMI-773, Oct. 15, 1952.
27. Denver Hale, Quarterly Progress Report, Report MLM-570, pp. 51-53, June 18, 1951.
28. R. N. Augustson, R. W. Endebrock, David C. Hale, and H. L. Rawlings, Quarterly Progress Report, Report MLM-535, pp. 26-28, Feb. 26, 1951.
29. Denver Hale, Quarterly Progress Report, Report MLM-602, pp. 40-42, Aug. 6, 1951.
30. J. M. Goode, Metal-Polonium Compounds, Report MLM-677, Apr. 1, 1952.

Chapter 9

INSTRUMENTATION

By Warren L. Hood and Adrian J. Rogers

1. INTRODUCTION

During the early years of the Dayton Project the radiometric assay of raw materials and polonium process solutions relied on those instruments which were available. At that time the Geiger counter, the Lauritsen electroscope, the alpha monitor, and the pulsed parallel-plate ionization chamber constituted the only available equipment that could be used for these purposes. Since that time a great variety of radiation assay and monitoring equipment has become commercially available. This chapter will describe the equipment which was developed (or modified) at the Dayton Project and Mound Laboratory to satisfy the existing needs of the polonium purification process.

2. HISTORICAL

2.1 *General.* Among the major uncertainties in the polonium purification process was the purity of the polonium produced and the efficiency of the various chemical separation procedures. Special instruments were developed to resolve these and other problems. Some of these instruments were used for only a short time and then discarded as techniques of measurement were improved, purification procedures were changed, and better instruments were developed. Other instruments, because of their versatility and general utility, were retained and developed to their present state of usefulness. This section will describe some of the instruments of historical interest which were used in the early days of the polonium project.

2.2 *Alpha Monitor.* One of the instruments used for the alpha assay of active samples of polonium in the early days of the Dayton Project was a large parallel-plate ionization chamber connected to a battery-powered electrometer circuit. The response of this instrument is a function of the intensity of the sample up to a disintegration rate of about 10^7 dis/min. The lower limit of sensitivity was about 10^4 dis/min owing to the masking of weak signals by background noise. This instrument, shown in Fig. 9.1, was designated the alpha monitor.

The alpha monitor, together with the hemispherical chamber described in Sec. 2.3, was used extensively for the assay of active samples until the development of successful low-geometry attachments for the Simpson counter (Sec. 3.1). The alpha monitor was used occasionally through 1952.

The alpha monitor underwent several stages of modification[1] to attain greater circuit stability and freedom from microphonics and to adapt it to a regulated a-c power supply. The a-c-powered circuit was sufficiently stable to give accuracy and reproducibility to within ±4 per cent.[1]

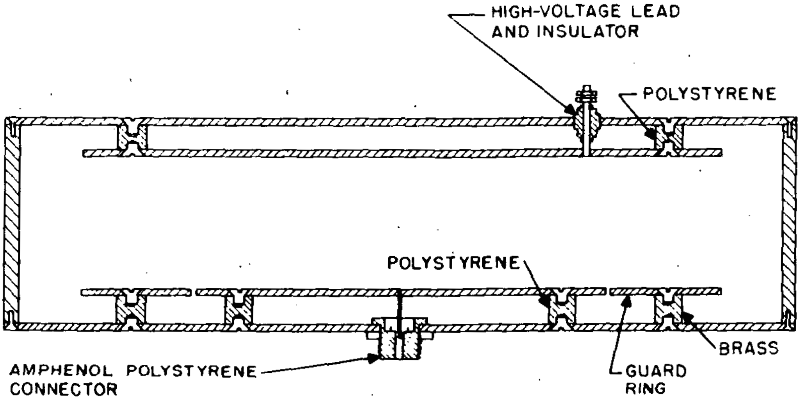


Fig. 9.1—Alpha monitor, cross section.

2.3 *Hemispherical Ionization Chamber (Sopkometer).* The alpha monitor described in Sec. 2.2, when operated at atmospheric pressure with air as the filling gas, was reliable up to a disintegration rate of only 10^7 dis/min because of recombination effects. A hemispherical ionization chamber operating at reduced pressures was developed by Sopka[2] for assaying millicurie amounts of polonium. This chamber, which consisted of a 1-liter spherical flask, is illustrated in Fig. 9.2. The sample was placed near the center of the spherical flask, and the counting volume was essentially hemispherical. This flask was provided with stopcocks for evacuation and filling. The high-voltage electrode was formed by evaporating a film of copper or gold on the inner surface of the flask. The other electrode was attached to the sample holder which was mounted on the male section of the ground joint. This electrode was machined to hold the 1-in.-square glass slides upon which the samples were mounted. The chamber was operated with air at a pressure of 15 cm Hg. At this pressure the recombination effects were negligible, and the chamber response was essentially linear up to at least 10^{10} dis/min.

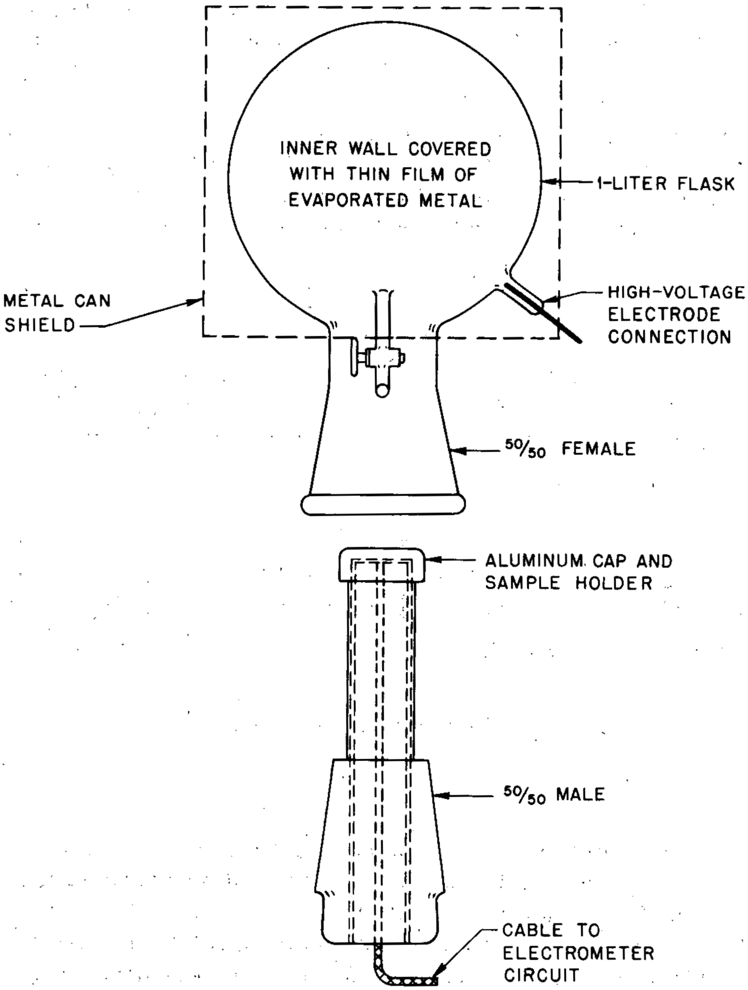


Fig. 9.2—Airtight spherical ionization chamber.

2.4 *Ionization Chamber for Assay of Bismuth Slugs.* An alpha ionization chamber, Fig. 9.3, was designed for the direct assay of active nonjacketed bismuth slugs.[3] The high-voltage electrode was a brass cylinder concentric with the cylindrical slug. The slug served as the second electrode and was connected to the electrometer circuit. The slug was placed in the cuplike plug, and both were inserted into the chamber from the bottom. The counting procedure involved comparing the unknown slugs with a number of slugs which had been chemically analyzed for use as standards. The use of this chamber was feasible only with slugs of low gamma flux.

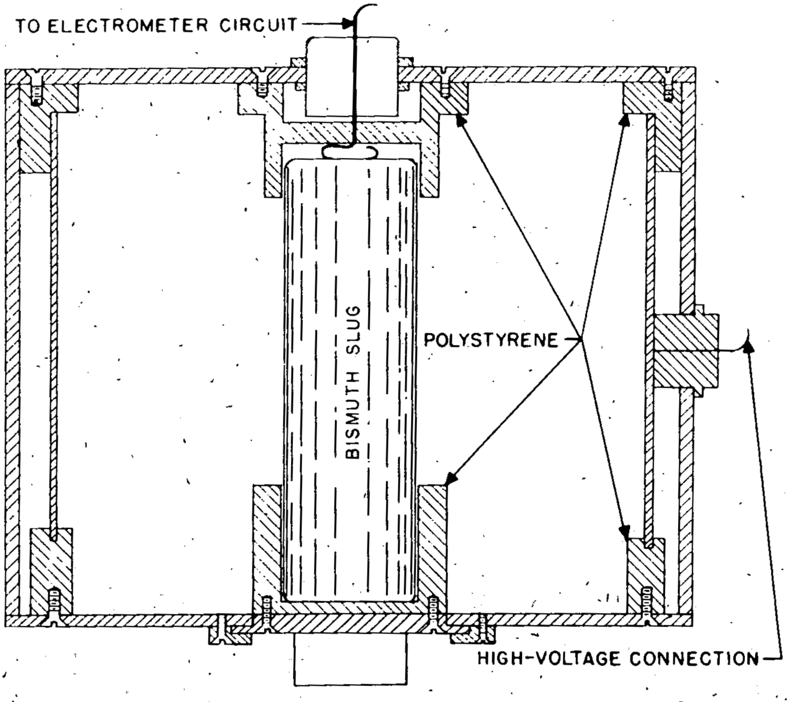


Fig. 9.3—Ionization chamber for alpha assay of bismuth slugs.

2.5 *Pencil-type Ionization Chamber.* A cylindrical ionization chamber[4,5] similar to an end-window Geiger counter was designed for determining the rate of depletion of polonium solutions during electrolysis (Fig. 9.4).

The chamber consisted of a length of 18-gauge platinum wire mounted in the center of a platinum cylinder. A polystyrene plug at one end of the chamber insulated the electrodes from each other and served as a spacer to maintain a concentric assembly. The lower (or collecting) end of the chamber was open. A positive potential of 135 volts was applied to the cylinder. The center electrode was connected to an electrometer circuit through a polystyrene beaded cable. This circuit was identical to the two-stage a-c-powered amplifier used with the alpha monitor.

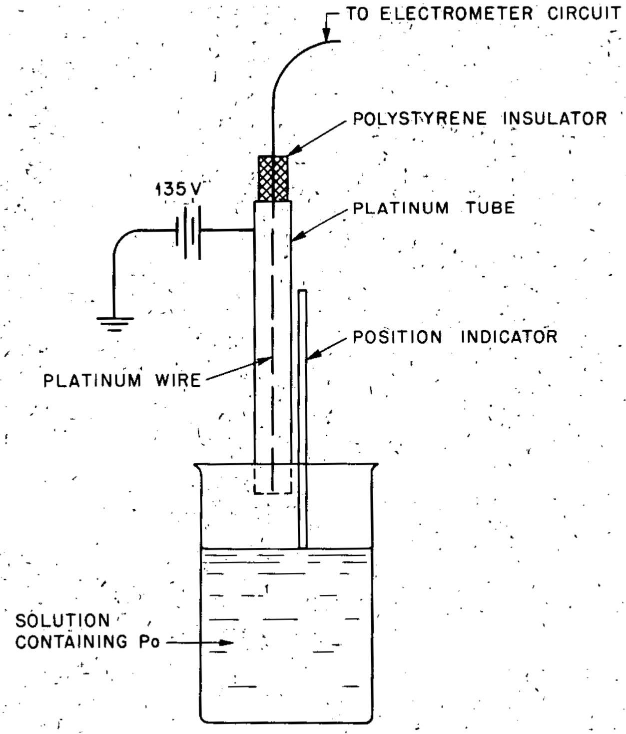


Fig. 9.4 — Pencil-type ionization chamber.

A measurement was made by lowering the chamber to some predetermined height, generally ¼ in., above the solution level and taking a reading with the electrometer. A polystyrene rod attached to the outside of the chamber and extending ¼ in. below it served as a chamber-to-solution distance indicator. Attempts to calibrate the ionization chamber were unsuccessful owing to contamination of the chamber and difficulty in maintaining a constant geometry.

3. RADIATION MEASURING INSTRUMENTATION

3.1 *Logac-S and Logac-L Alpha Counters*. Two low-geometry attachments were developed$^{6-8}$ to adapt the methane-flow proportional alpha counter (Simpson counter[9]) to the measurement of alpha-emitting samples whose activity range falls between the upper limit of the Simpson counter and the lower limit of the calorimeter (2×10^5 to 10^{10} dis/min).

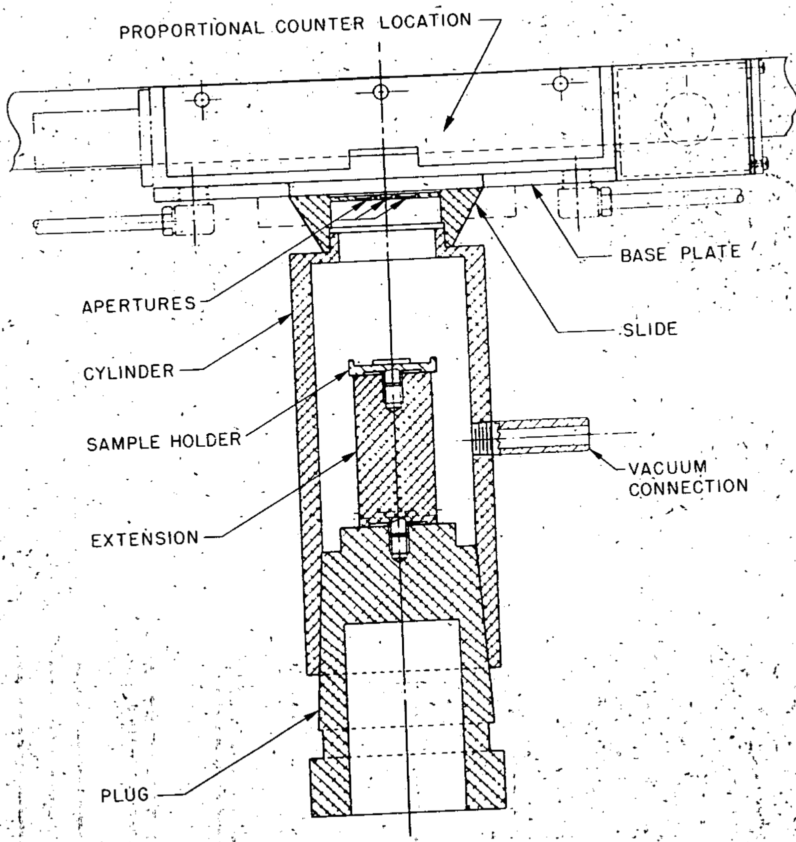


Fig. 9.5—Logac-S assembly.

The shorter low-geometry attachment, designated as the "Logac-S," covers the range from 10^5 to 10^9 dis/min. It is designed to be attached to a proportional counter without alteration of the counter other than to space the counting chamber away from the front panel of the scaler and to replace the slide and base plate with similar parts drilled with holes to define the geometry of the counter. Figure 9.5 shows an assembly drawing of the Logac-S. Figure 9.6 shows the Logac-S installed on a Nuclear Instrument & Chemical Corp. version of the Simpson counter.

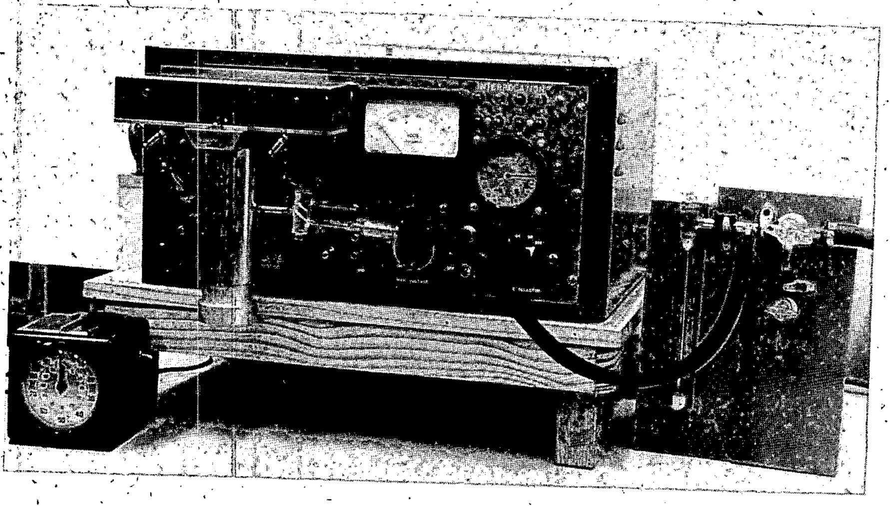


Fig. 9.6—Logac-S installed.

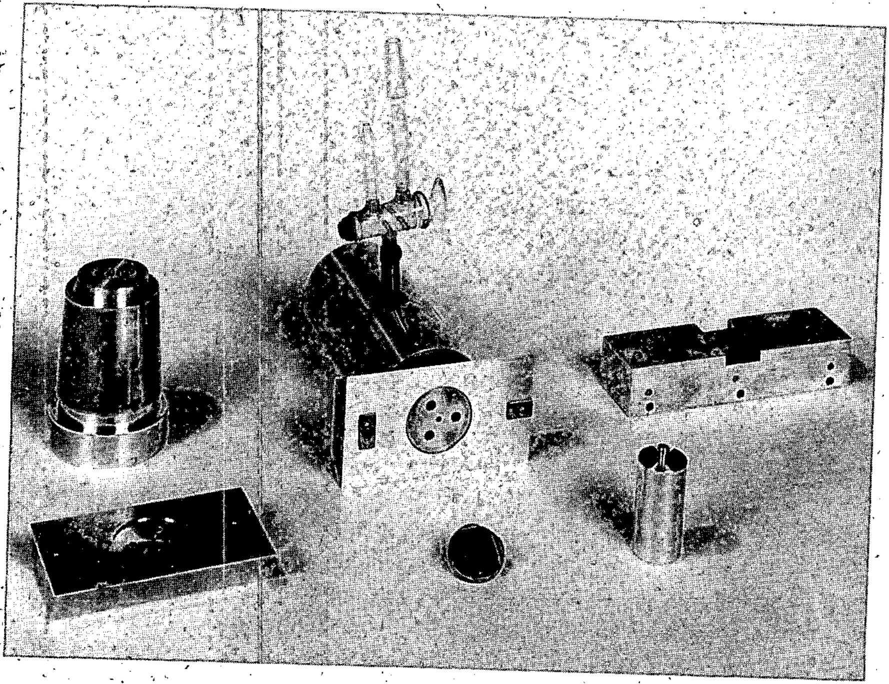


Fig. 9.7—Logac-S disassembled.

The Logac-S consists of seven parts, a base plate (not shown), slide, sample holder, spacer, extension, cylinder, and plug, as illustrated in Fig. 9.7.

Three geometry factors of approximately 4×10^2, 1.5×10^3, and 1.5×10^4 can be obtained by changing the spacing between the sample and the apertures and by shifting the position of the gate slide with respect to the base plate to align either one or four of the geometry-defining apertures in the slide and base plate. A fourth geometry factor is possible, but it is essentially a duplicate of one of the other configurations. The geometry factor for each configuration is calculated by counting accurately measured standards.

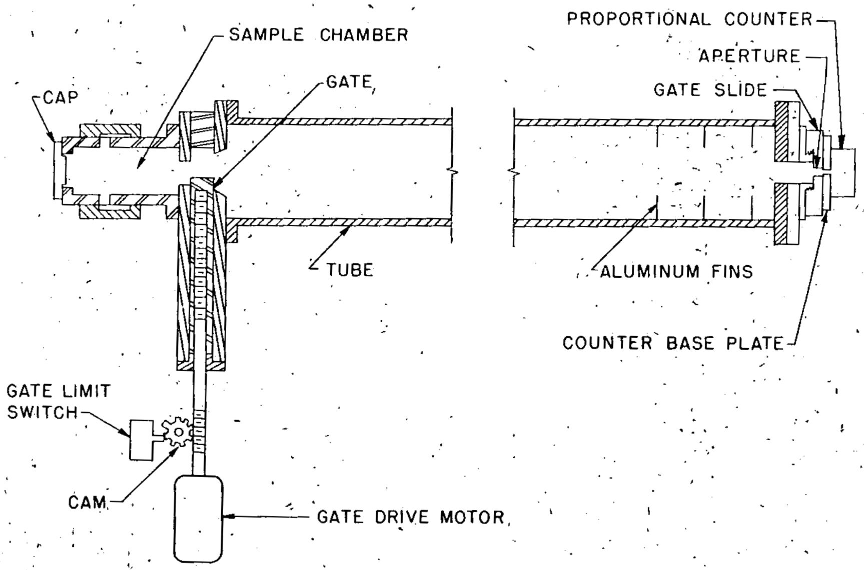


Fig. 9.8—Schematic representation of Logac-L.

A thin sheet of mica (1.5 to 2.0 mg/cm^2) is cemented over the four apertures in the counter base plate to obtain a vacuumtight alpha-transparent seal between the gas-filled counter and the evacuated Logac-S attachment. DeKhotinsky cement is used to cement the mica in place.

The longer low-geometry attachment, designated as the "Logac-L,"[6] is designed to count samples in the range of 10^9 to 10^{13} dis/min. The very low geometry is attained by making the sample-to-aperture spacing approximately 80 in. and by using an even smaller aperture area at the proportional counter than is used with the Logac-S. A schematic diagram of the Logac-L is shown in Fig. 9.8. Figure 9.9 shows an installation of two Logac-L attachments.

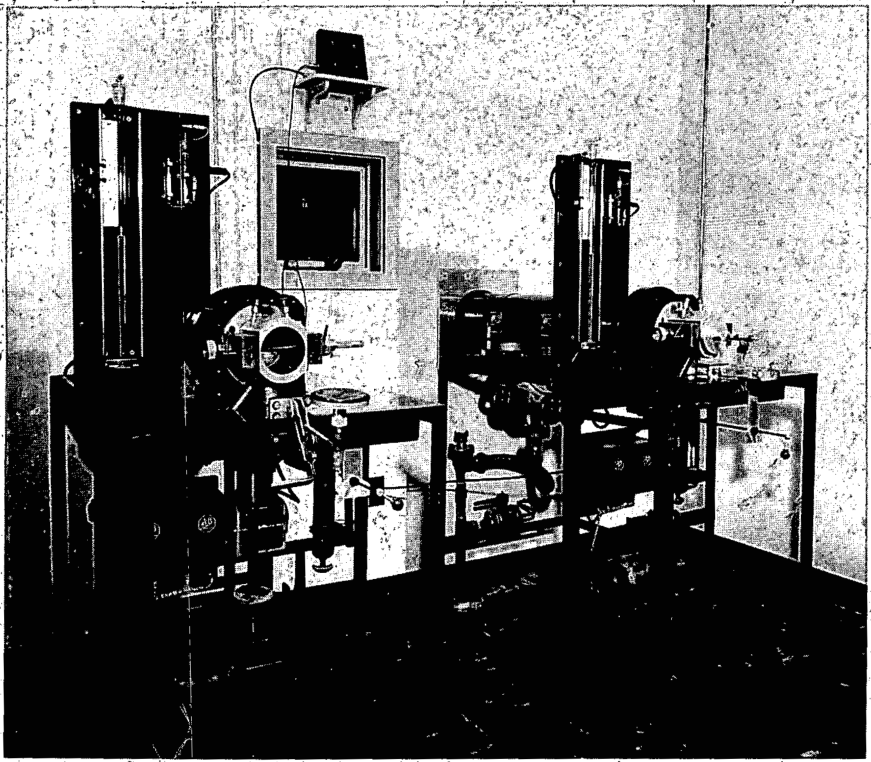


Fig. 9.9—Logac-L installation (loading end).

The geometry-defining assembly consists of a brass tube 6 ft long and 8 in. in diameter with a proportional counter and a sample chamber attached to its opposite ends. The geometry of this system may be changed by a factor of approximately 10 by shifting the position of the proportional counter with respect to the dovetailed slide to align either one or four of the holes in the slide with the corresponding holes in the base of the counter.

The Logac-L is equipped with its own vacuum system and mercury manometer. A motor-actuated gate, located between the tube and the sample chamber, and separate solenoid valves in the vacuum lines to the sample chamber and the tube make it possible to evacuate either the entire Logac-L or the tube alone. Thus the time required for admitting a sample for counting is greatly reduced because the vacuum may be maintained in the tube and only the sample chamber will require reevacuation. The gate is equipped with switches to limit its travel between the open and closed positions and to actuate a solenoid valve when the gate is closed to admit air into the sample chamber. A contact-making manometer connected in series with the gate control circuit prevents reopening of the gate until the sample chamber is completely reevacuated.

Counting operations which involve the use of the gate are generally accomplished by admitting samples through a circular port at the rear of the sample chamber. This port is covered by a gasketed cap attached to an over-center clamping device consisting of a commercial jig clamp. The port may be quickly opened or closed by rotating the clamp handle through an angle of about 60 deg. Samples may be attached to the cap by means of tapped holes on its inner face.

For the routine alpha counting of polonium deposited on platinum microfoils (Chap. 7, Sec. 11.2), the sample chamber is equipped with two mounting blocks designed to receive the special foil holders (Sec. 4.6) used in the electroplating and weighing of polonium during the purity assay. A mounting block is located on each side of the sample chamber as shown in Fig. 9.9. A foil holder is installed in the right-hand mounting block of the left-hand Logac-L of Fig. 9.9. A microfoil is shown held in the forceps of the foil holder with the foil extended in counting position. These mounting blocks together with the foil holders make it possible to introduce the microfoils into the sample chamber without bringing the chamber up to atmospheric pressure.

The Logac-L is equipped with a lamp (to illuminate the interior of the sample chamber) and a window (located on top of the chamber) through which the foil may be observed when in counting position.

Gross contamination of the interior of the sample chamber and the tube is prevented by lining the sample chamber with a brass sleeve which has a rubber hydrochloride window cemented across the end toward the tube. The sleeve is provided with holes which align with the ports in the sample chamber. The sleeve is easily removed through the large gasketed port at the rear of the sample chamber for sleeve decontamination or replacement of the rubber hydrochloride window.

In a more highly developed model of the Logac-L, a rotating sample holder is incorporated within the sample chamber in order that a sample may be continuously rotated while it is being counted. This particular instrument is also equipped with a Cartesian monostat (Emil Greiner Co.) which will maintain a pressure constant to within ±0.1 per cent within the Logac-L for the purpose of making absorption studies.

Counting inaccuracies due to the scattering of alpha particles from the surface of the tube are prevented by means of a series of spaced aluminum fins located within the tube.

The geometry factor for the Logac-L is determined by comparison to calorimetric measurements of foils, each of which has about 3 curies of polonium deposited upon it. This amount of polonium can be measured accurately with the calorimeter.

The Logac-L is installed in the laboratory in which the samples are prepared, and the proportional counter end extends through the wall into the counting room. Contamination of the counting room by active samples is thus prevented.

3.2. *Measurement of Radioactivity with a Radioelectric Cell.*[10-12]

(a) *Principle of Operation.* If two electrochemically dissimilar materials are separated by a normally nonionized medium, a current will flow through an external circuit connected between the two materials when the separating medium is forcibly ionized upon exposure to radiation. The magnitude of this current depends upon the load impedance, the type and intensity of the ionizing radiation, the contact potential difference between the materials, the type and pressure of the filling gas, and the geometry of the cell. If the ionization is due to gamma radiation, the current also depends upon the gamma-absorbing properties of the electrodes and the filling gas. If the ionization is due to neutron radiation, the current depends upon the effectiveness of the electrodes and the filling gas in producing ionizing particles by interaction with neutrons.

Although this phenomenon, which was designated as the "radioelectric effect," was discovered independently at Mound Laboratory, it was first demonstrated by Kelvin.[13] Cells utilizing this principle for counting radioactive emissions are called "radioelectric cells."

The radioelectric cell can be considered as analogous to an electrochemical cell in which the open-circuit potential is the difference in the work functions of the two electrode surfaces and the source of energy is the ionizing radiation. Since the formation of a positive ion is a loss of electrons and hence an oxidation, and since the neutralization of a positive ion is a gain of electrons and hence a reduction, the current from a radioelectric cell can be considered as coming from an oxidation-reduction reaction. However, this oxidation-reduction involves the filling gas and does not imply any permanent valence change in the oxidation state of the electrodes themselves. Also, the energy to produce this oxidation and reduction comes from outside the cell.

The radioelectric effect may be used for the detection of alpha, beta, gamma, and neutron radiation. Experimental cells have been built for neutron detection, and several types of gamma-detecting cells have been designed and built with which gamma radiation can be measured with high precision.

(b) *Cell Characteristics.* Table 9.1 shows the open-circuit (characteristic) potentials of specific cells with an aluminum oxide negative electrode and various other materials as the positive electrode. It will be noted that the potential differences generally tend to fall in the same order as the work functions of the elements. There are exceptions, which would be expected if the characteristic potentials are a measure of the difference in the work functions of the surfaces, since in most cases those surfaces are oxides (or other compounds) rather than the pure elements. The thickness of the surface also affects the charac-

Table 9.1—Characteristic Potentials of Specific Cells with Aluminum (Al_2O_3) Negative Electrodes

Test electrode	Open-circuit voltage, volts
PbO_2 plated on gold	1.34
Carbon (aquadag-coated aluminum)	1.01
Copper oxide on copper	0.975
Gold plated on copper	0.95
Brushed gold plated on copper	0.945
Copper	0.72
Silver	0.67
Brushed copper	0.64
Nickel	0.63
Brass	0.58
Stainless steel	0.57
Brushed brass	0.425
Sanded nickel	0.41
Nickel, 1% cobalt (plated)	0.41
Sanded stainless steel	0.39
Zinc	0.32
Lead	0.22
Brushed lead	0.20
Chromium (plated)	0.18
Cadmium (plated)	0.132
Cadmium	0.06
Sanded cadmium	0.026
Sanded zinc	−0.01
Aluminum (1 min after sanding)	−0.32

teristic potential. If the surface is thin, the characteristic potential may have a value intermediate between the one it would have with a "thick" surface film and the one it would have with a surface of the pure element. The characteristic potential is independent of the type of radiation.

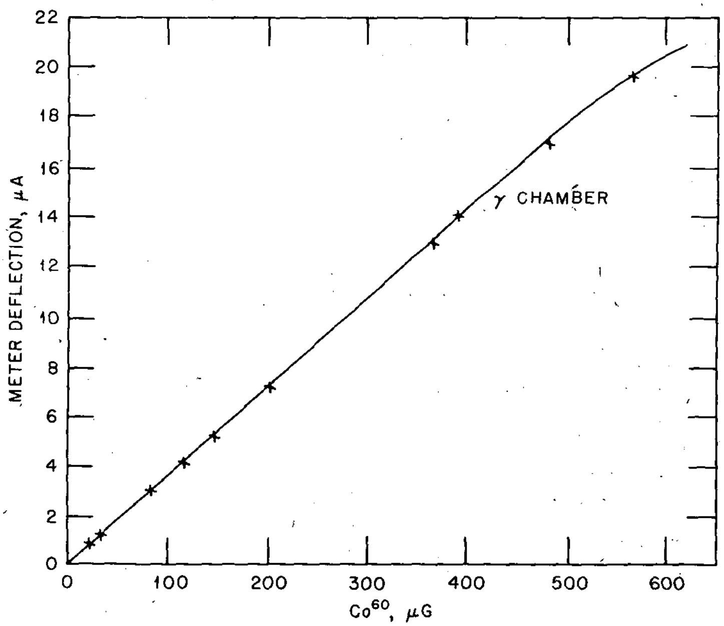


Fig. 9.10—Calibration curve for a simple coaxial radioelectric cell.

The linearity of the radioelectric cell is shown by the calibration curve for a simple coaxial cell with electrodes of magnesium oxide and lead dioxide, Fig. 9.10. This cell was connected to a single-tube electrometer circuit and calibrated with several Co^{60} gamma sources.

The pressure vs. current characteristics of several gases in a parallel-plate high-pressure gamma-sensitive radioelectric cell are shown in Fig. 9.11. The current increases as the density of the filling gas increases. The linearity of curves of this type is greatly affected by the spacing between adjacent electrodes.

The pressure vs. current characteristics for a neutron-sensitive radioelectric cell with hydrogen as the filling gas are shown in Fig. 9.12. The cell used in these experiments was a multiple electrode, coaxial type, similar to the one shown in Fig. 9.15. The cell characteristics using electrodes with polyethylene cores are shown. A control set of electrodes (aluminum oxide and carbon-on-aluminum) also was tested in order that an approximate determination could be made of the contribution of the hydrogenous core material. The addition of the hydrogenous core increased the neutron-detection efficiency and the neutron-to-gamma discrimination.

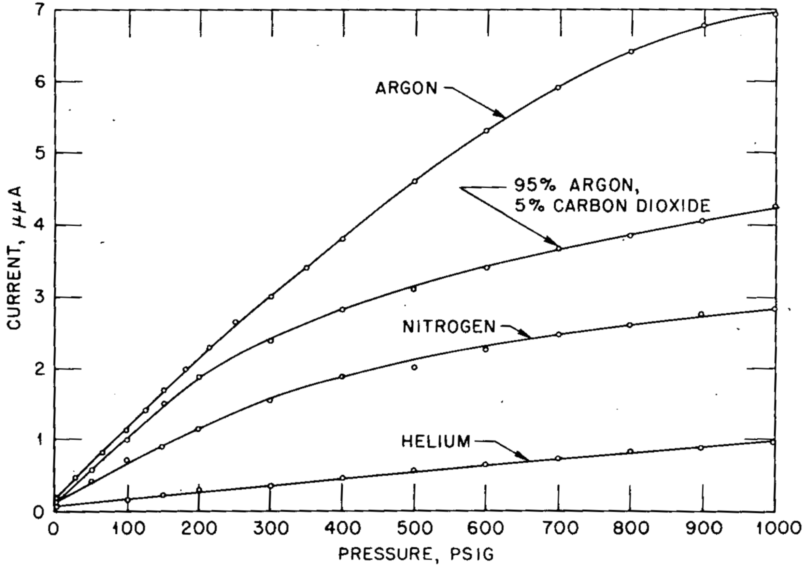


Fig. 9.11—Pressure vs. current for a high-pressure gamma-sensitive radioelectric cell.

(c) *Application.* The first practical instrument that was constructed using the radioelectric effect was a gamma survey meter shown (with batteries removed) in Fig. 9.13. This instrument is approximately equivalent to the pistol-type survey meter known as "Cutie Pie." The positive electrode was made by plating gold on copper and coating the gold with lead dioxide. The negative electrode was made by plating lead on the inside of the brass cell case and evaporating aluminum on the lead. The dimensions of the instrument are $3\frac{1}{8}$ by $3\frac{1}{8}$ by $7\frac{1}{4}$ in., which is slightly larger than the ionization chamber of the Cutie Pie.

A pocket dosimeter, Fig. 9.14, which utilizes the radioelectric effect was also constructed. It consists of a cylindrical capacitor whose electrodes support the concentric cylindrical electrodes of a radioelectric cell. The capacitor is initially uncharged and acquires a charge that is

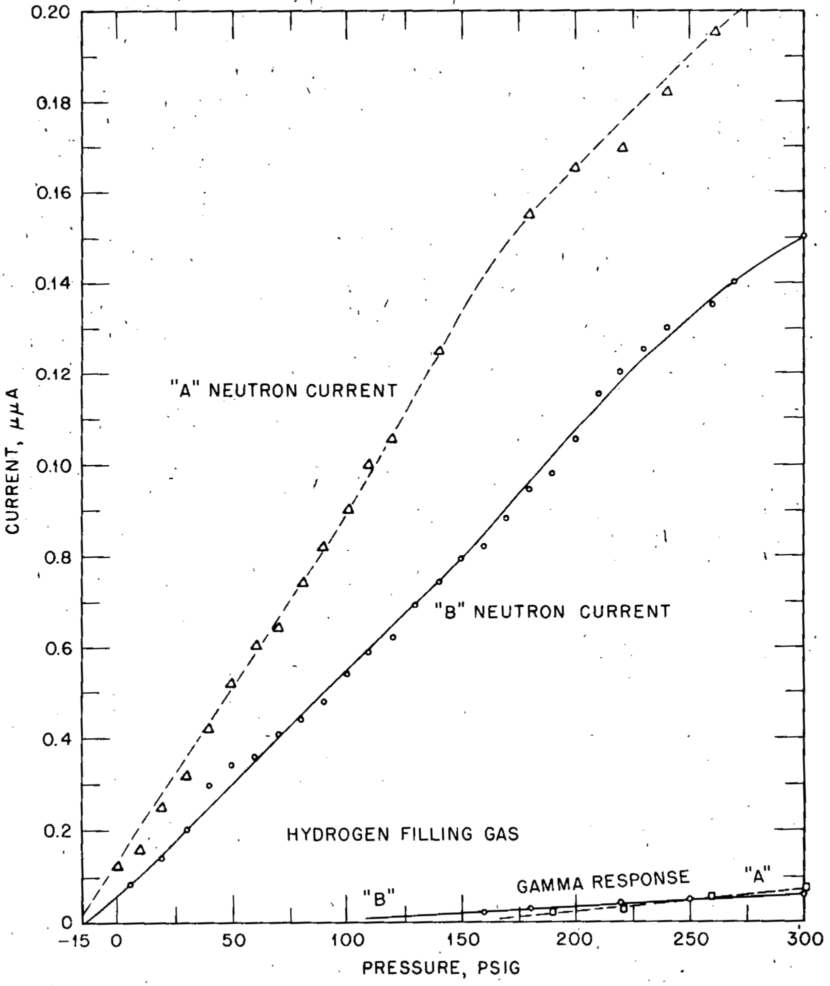


Fig. 9.12 — Pressure vs. current for a neutron-sensitive coaxial radioelectric cell. A. Carbon conductive paint on 0.010-in. polyethylene, positive electrode; 0.0005-in. aluminum foil on 0.010-in. polyethylene, negative electrode. B. Carbon conductive paint on 0.003-in. aluminum foil, positive electrode; 0.003-in. aluminum foil, negative electrode.

proportional to the total ionizing effect of the flux passing through the cell. The cell is hermetically sealed in an inert atmosphere and should retain its electrical characteristics indefinitely. There is a tendency for the capacitor to be discharged by the radiation, but this is mini-

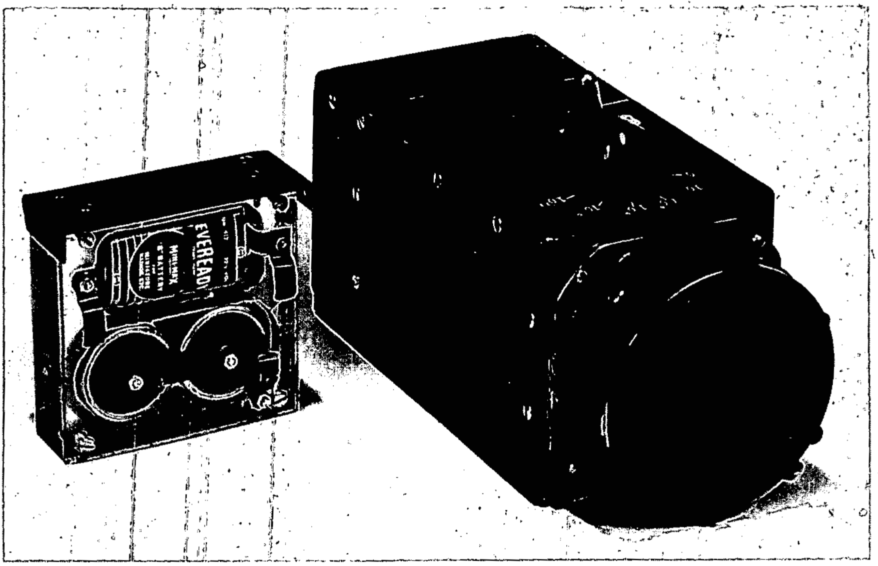


Fig. 9.13—Radioelectric gamma survey meter.

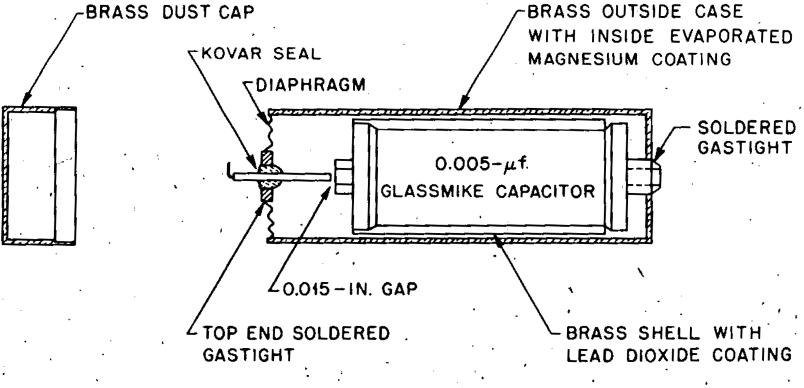


Fig. 9.14—Radioelectric pocket gamma dosimeter.

mized by making the capacitor electrodes of the same material and by using a solid dielectric. The potential (or charge) of the capacitor may be read by depressing an external electrode (a Kovar seal mounted on the flexible diaphragm in the end of the dosimeter) to make contact with the ungrounded electrode of the cell. A metal cap covers this electrode during normal use of the dosimeter to complete the electrical shielding of the capacitor and to prevent its accidental discharge.

Several types of quantitative gamma detectors utilizing the radioelectric effect have been designed and built. These instruments have supplanted the Geiger counter for the assay of polonium by gamma counting in some phases of the polonium-from-irradiated-bismuth process. For example, a multielectrode coaxial cell of the type shown disassembled in Fig. 9.15 has been used for the gamma assay of polonium plated on platinum foils and gauzes. The instrument previously used for this purpose is the rotating-source gamma chamber described in Sec. 3.5. This counter gives a satisfactory gamma assay of unsymmetrical sources, but long counting times are necessary because of the low geometry. During a run of 165 measurements with both instruments, the radioelectric cell used in conjunction with a very simple electrometer circuit gave a precision of 1.5 per cent, and the rotating

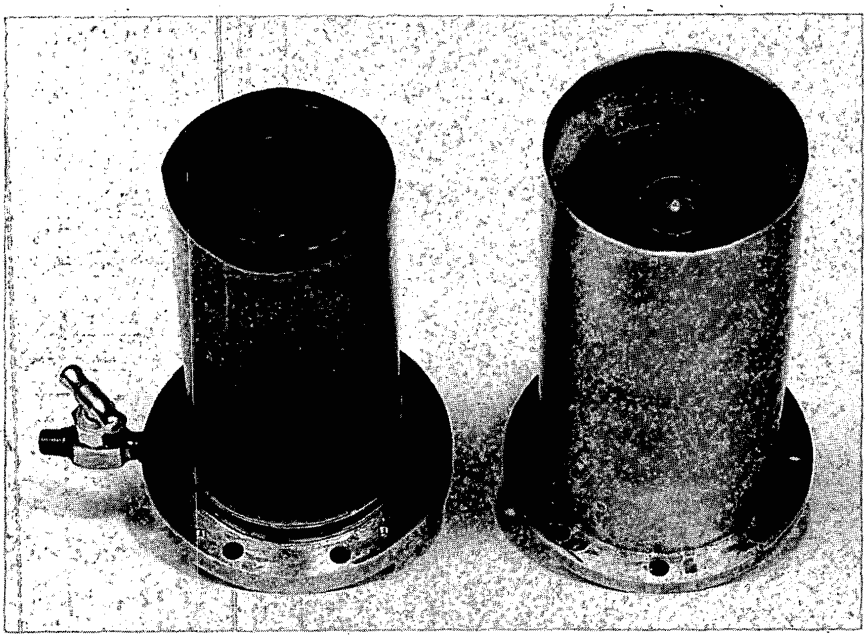


Fig. 9.15—Multielectrode coaxial cell, disassembled.

gamma counter gave a precision of 1.8 per cent (see reference 14). The radioelectric instrument required only a fraction of the time required by the rotating gamma counter to make a measurement, yet it was at least equally precise. The precision attained with the radioelectric instrument was essentially the precision of reading the 3-in. panel meter of the electrometer.

A recent design of a radioelectric instrument consisting of a coaxial cell, a sensitive electrometer and indicating unit, and a battery power supply is shown in Fig. 9.16.

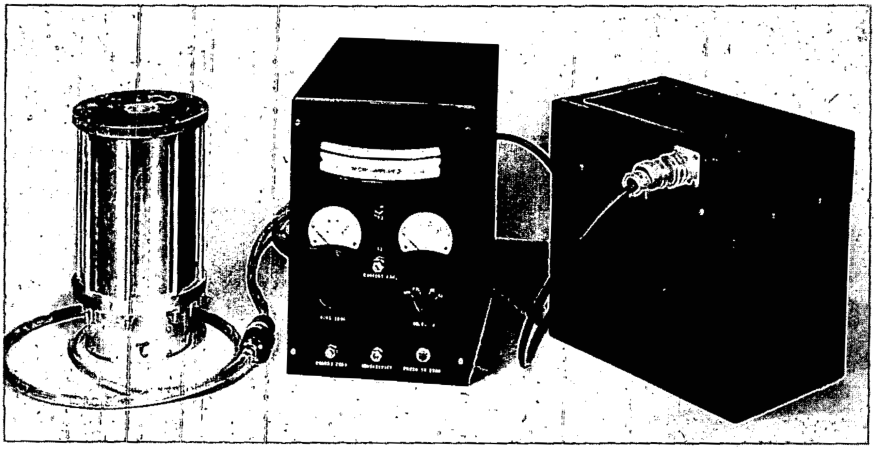


Fig. 9.16—Radioelectric process monitor.

(d) *Design Considerations.* The combination of characteristics which are unique to the radioelectric cell makes it possible to design cells of high stability which will measure a wide range of radiation intensities with good linearity. It is also possible, generally, to adapt the design to a particular radiation-detection problem, owing to the wide choice of available electrode materials, filling gases, and cell configurations.

Since the radioelectric cell is an integrating device which responds to average ionization current, its operating range is not limited by resolving time. Cells may be designed with closely spaced electrodes with large surface areas to attain high sensitivity with minimum cell volume, with a resultant reduction in the statistical fluctuation of cell current due to the increased capacitance.

The radioelectric cell requires no external ionizing potential because the contact potential difference between electrodes is used for ion collection. The problem of insulating the electrodes from each other is thereby greatly reduced, and closely spaced electrodes may be used to attain increased sensitivity.

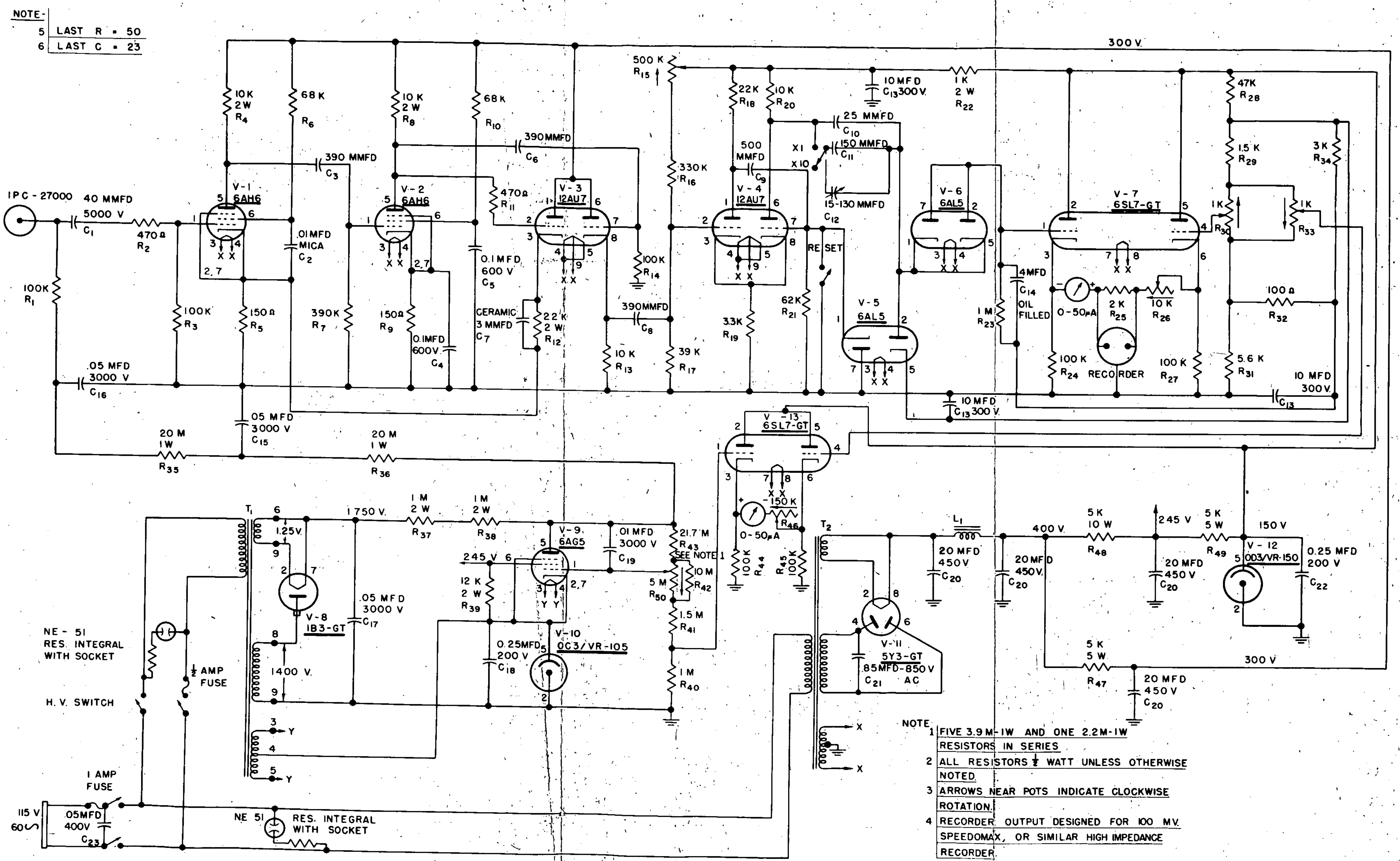
A cell of almost any configuration is satisfactory since point electrodes and high potential gradients are not required for the satisfactory operation of a radioelectric cell. In general, cells may be designed to conform to the form and size of the sample. For example, a coaxial cell might be used to measure the total radiation from a small sample or to monitor a radioactive fluid in a pipe, whereas a cell in the form of a probe might be used for exploring a small volume.

The wide choice of electrode materials and filling gases available makes it possible to design cells with particular operating characteristics, such as maximum sensitivity to one type of radiation, maximum discrimination against a certain type of radiation, maximum stability, or maximum characteristic potential.

3.3 *Neutron Counters*. Polonium alpha particles react with a number of light elements to produce neutrons. The occurrence of these elements in the polonium purification process, either as impurities or as process constituents, is a potential source of hazardous neutron radiation. Instruments for continuously monitoring the various phases of the polonium process for neutron radiation and for the routine assay of neutron sources have been developed to a status consistent in precision with the measurement of other nuclear particles.

A fast-neutron monitor utilizing a boron-lined proportional counter and a paraffin moderator was developed to detect the fast neutrons produced by (α,n) reactions in the polonium process. The counter and moderator are usually placed in a position corresponding in neutron-flux density to that in the vicinity of the worker. Where the polonium process operations are performed in closed hoods, the counter and moderator are usually located inside the hood against the panel separating the work from the worker.

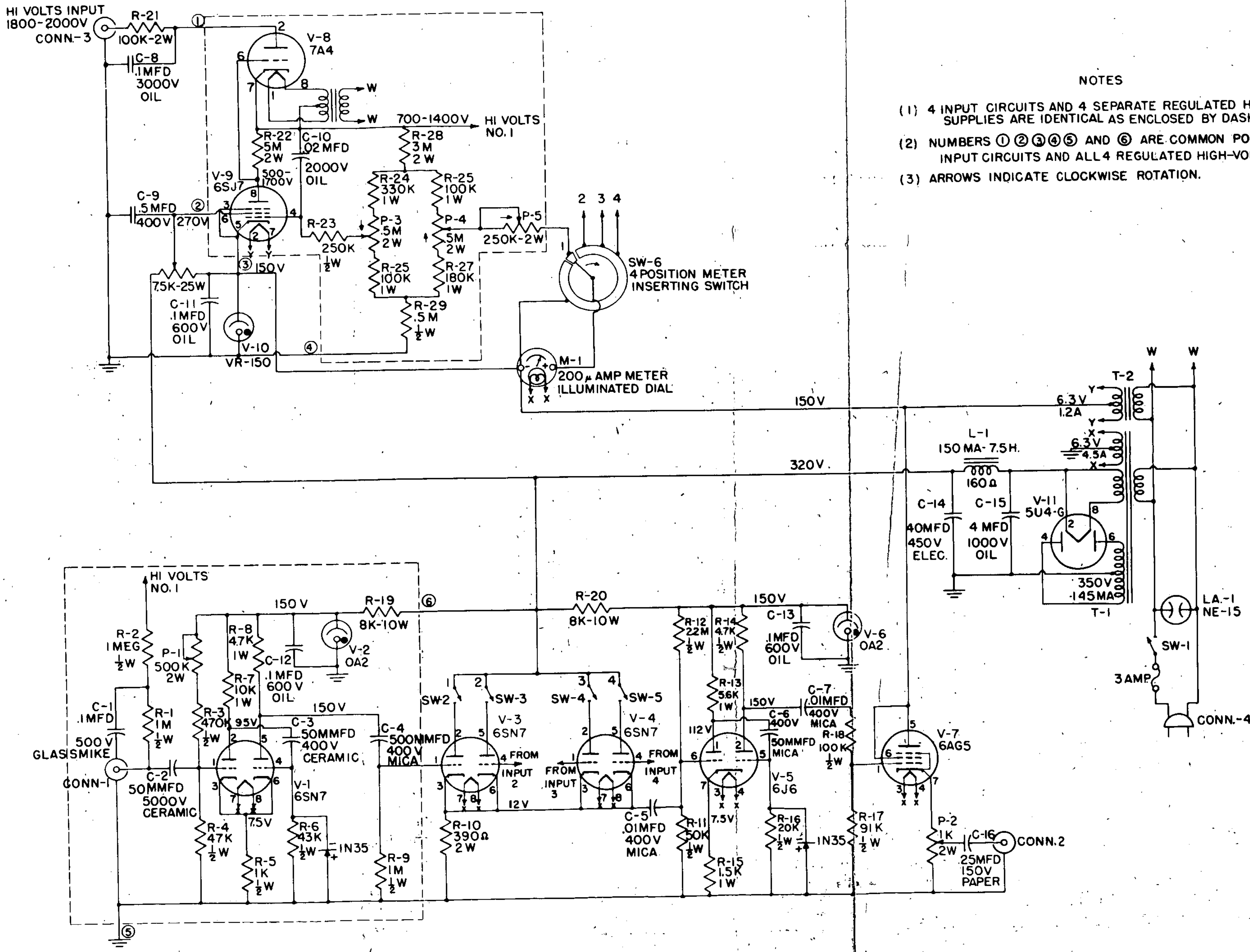
The fast-neutron monitor shown schematically in Fig. 9.17 consists of a linear pulse amplifier (V-1, V-2, and V-3), a pulse generator (V-4), and a pulse rate meter (V-5, V-6, and V-7). The monitor is located near the working area; consequently the calibrated rate meter is conveniently observed. The rate meter has a linear scale having a full-scale reading of 50 counts/sec. A multiplier switch which is located on the front panel of the monitor permits a factor of 10 increase in the rate-meter scale reading. An outlet is provided in order that the rate-meter reading may be recorded on an auxiliary recorder. This recorder should have a full-scale sensitivity of 100 mv and an input impedance of at least 200,000 ohms.



NOTE-
5 LAST R = 50
6 LAST C = 23

NOTE
1 FIVE 3.9 M-1W AND ONE 2.2M-1W RESISTORS IN SERIES
2 ALL RESISTORS ½ WATT UNLESS OTHERWISE NOTED.
3 ARROWS NEAR POTS INDICATE CLOCKWISE ROTATION.
4 RECORDER OUTPUT DESIGNED FOR 100 MV. SPEEDOMAX, OR SIMILAR HIGH IMPEDANCE RECORDER.

Fig. 9.17—Fast-neutron monitor.



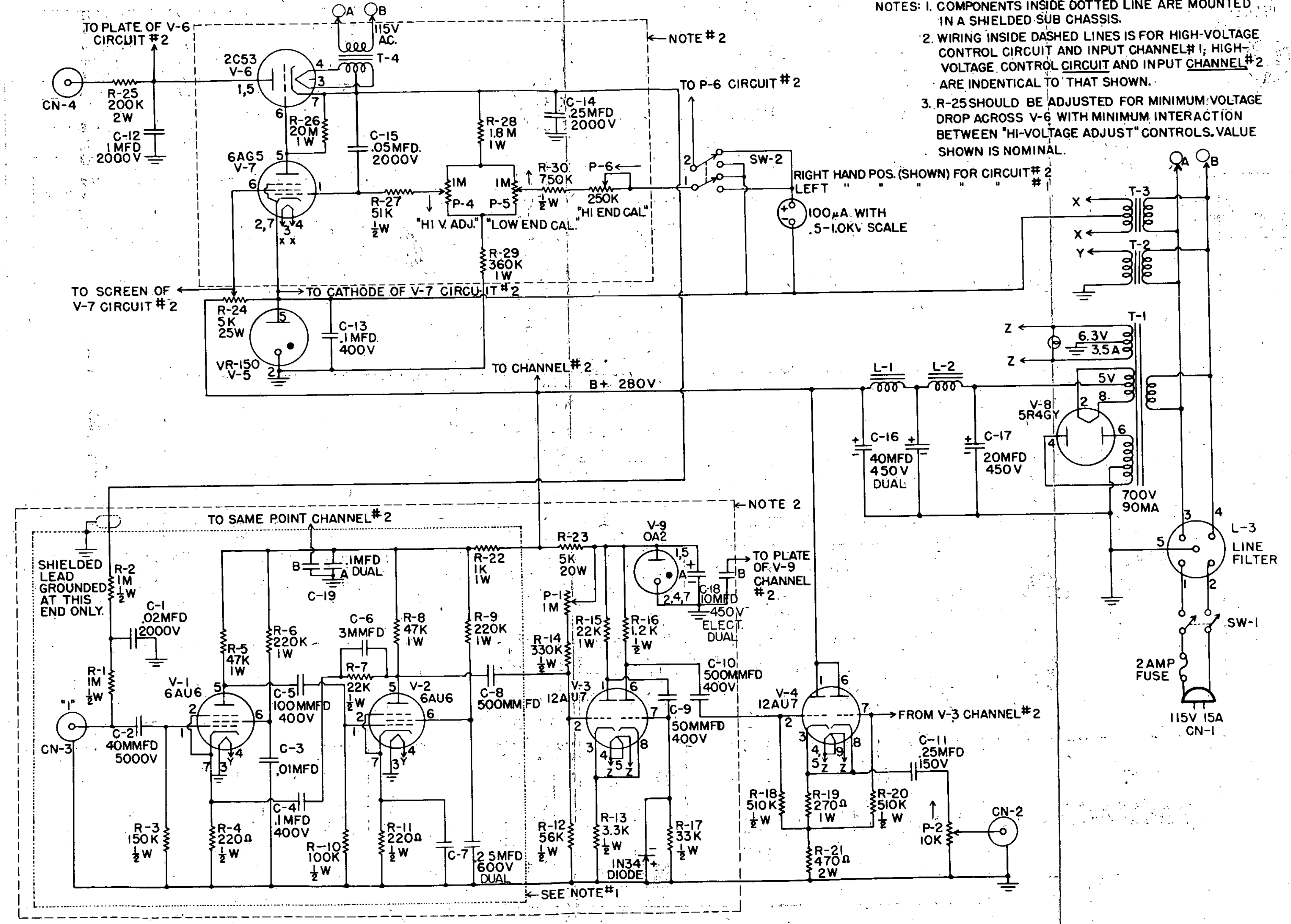
NOTES

(1) 4 INPUT CIRCUITS AND 4 SEPARATE REGULATED HIGH-VOLTAGE POWER SUPPLIES ARE IDENTICAL AS ENCLOSED BY DASHED LINES.

(2) NUMBERS ①②③④⑤ AND ⑥ ARE COMMON POINTS TO ALL 4 INPUT CIRCUITS AND ALL 4 REGULATED HIGH-VOLTAGE SUPPLIES.

(3) ARROWS INDICATE CLOCKWISE ROTATION.

Fig. 9.18—Four-input gamma mixer.



NOTES: 1. COMPONENTS INSIDE DOTTED LINE ARE MOUNTED IN A SHIELDED SUB CHASSIS.

2. WIRING INSIDE DASHED LINES IS FOR HIGH-VOLTAGE CONTROL CIRCUIT AND INPUT CHANNEL #1; HIGH-VOLTAGE CONTROL CIRCUIT AND INPUT CHANNEL #2 ARE INDENTICAL TO THAT SHOWN.

3. R-25 SHOULD BE ADJUSTED FOR MINIMUM VOLTAGE DROP ACROSS V-6 WITH MINIMUM INTERACTION BETWEEN "HI-VOLTAGE ADJUST" CONTROLS. VALUE SHOWN IS NOMINAL.

Fig. 9.19 — Two-input neutron mixer.

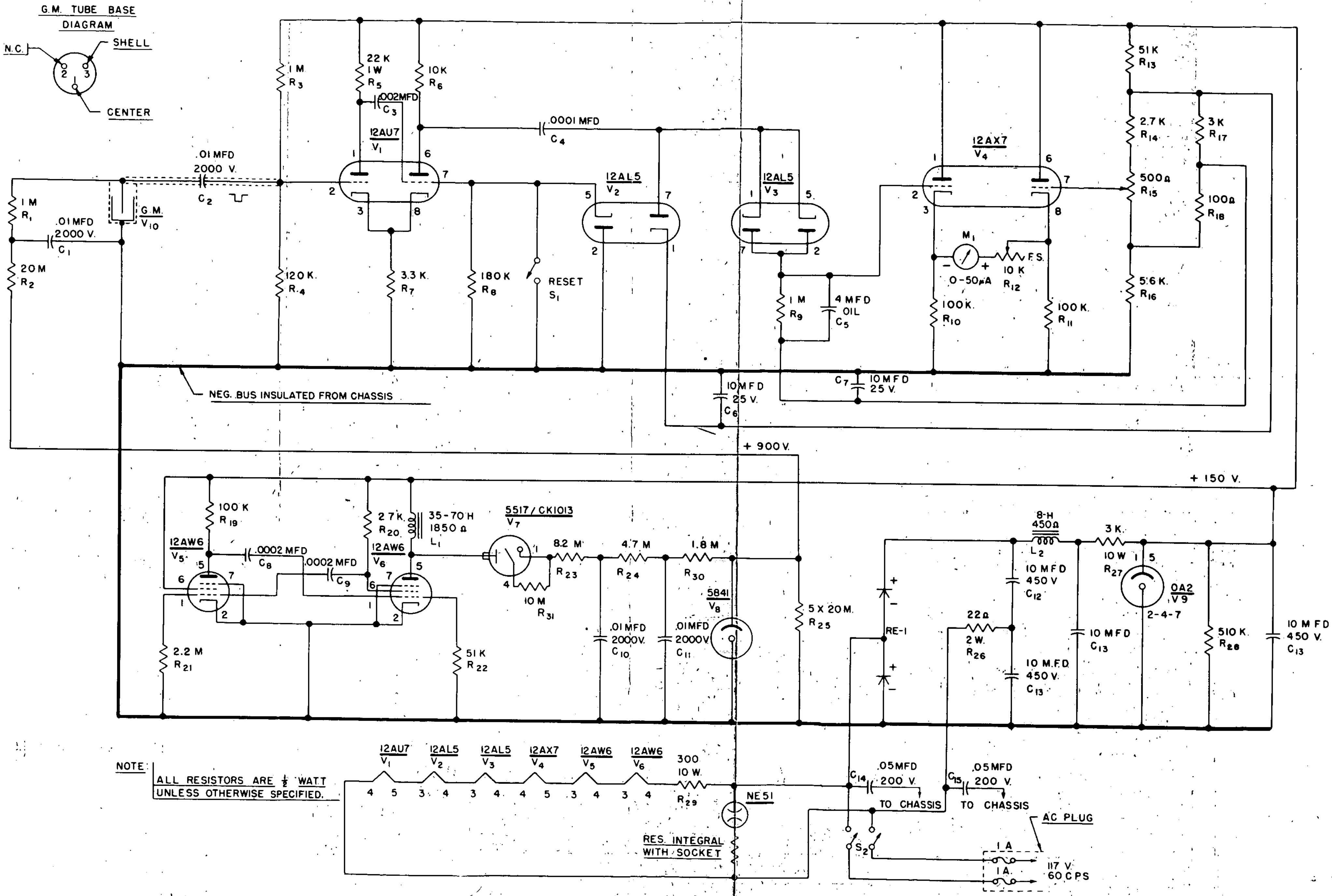


Fig. 9.22—Wall-mounting gamma monitor.

3.4 *Multiple-input Radiation Detectors.* (a) *Four-input Gamma Mixer.* Instruments were constructed at the Dayton Project which would combine the outputs of two, three, or four Geiger tubes and record the total counts with a single fast scaler. The original design of this instrument was completed by the Los Alamos Scientific Laboratory. These four-input gamma mixers were considerably more efficient than other existing counters for assaying nonhomogeneous sources; however, later instruments (Secs. 3.2 and 3.5) superseded this particular counter. The four-input gamma mixer is shown schematically in Fig. 9.18.

The version of this counter that was constructed at the Dayton Project differed from the instrument developed at the Los Alamos Scientific Laboratory by the following features:

1. Instead of using four separate identical radio-frequency power supplies for the Geiger tubes, four separate regulator circuits which were powered by a single transformer-rectifier-filter network were used.
2. The input sensitivities to each mixer stage were made variable to compensate for differences in pulse amplitude between Geiger tubes.
3. A simple switch network (not shown in this schematic) in the input grid of V-5 (Fig. 9.18) enabled the circuitry to be used for measuring gamma coincidences in either one, two, or three Geiger tubes with respect to the remaining tube or tubes.

The normal operation of this instrument consists in arraying the four Geiger tubes around the source holder in a uniform geometrical pattern. Gamma counting a nonhomogeneous source under these conditions will reduce the coincidence correction by a factor of 4. In addition, comparison of this instrument with conventional gamma counters shows that isotropic gamma sources can be counted with the same statistical precision in ¼ of the time.

(b) *Two-input B-wall Neutron Mixer.* An instrument for mixing the output pulses from two boron-lined (B-wall) neutron counter tubes and recording the mixed output on a single scaler has been developed at Mound Laboratory. Individually adjustable regulated high-voltage power supplies permit the operation of each B-wall tube in the best portion of its characteristic plateau. Two broad-band degenerative amplifiers (7×10^4 to 2×10^6 cycles/sec) and a twin-triode cathode follower constitute the mixing portion of this instrument. Each mixer channel has a maximum gain of 10 and will accept negative pulses up to a magnitude of 2 volts without clipping the pulse.[15] Figure 9.19 is a diagrammatical representation of the two-input B-wall mixer. A suppressed-zero-voltmeter circuit and a tapped cathode resistor for proper biasing of the mixer stage are features of this instrument.

3.5 *Rotating-source Gamma Chamber.* Inaccuracies in gamma counting due to nonhomogeneity of sources have given considerable trouble in sample assay. The four-input gamma counter (Sec. 3.4a) was effective in overcoming gross errors due to the nonhomogeneous properties of the source. A revolving-source gamma chamber was developed which defined a geometry for gamma counting such that a unit of activity produced the same response over a small range of source positions. This was accomplished by rotating the source mechanically to produce homogeneity about the axis of rotation and by interposing a hand-figured lead lens (Fig. 9.20) between the source and the Geiger tube to produce a flat response to a unit of activity along a portion of the tube length.

Through the use of the single Geiger tube and lead attenuator assembly shown in Fig. 9.21, one geometry can be used for the assay of a 1000-to-1 range of source activity.[16] The lead attenuator, when placed between the source and the Geiger tube, induces a flat response to an approximate point source over a 5-cm length parallel to the Geiger tube. The variation in response with the attenuator in position is less than 1 per cent, whereas without the attenuator the response varies up to 70 per cent over the 5-cm range. Empirical forming of the lead attenuator was necessary to achieve the desired results.

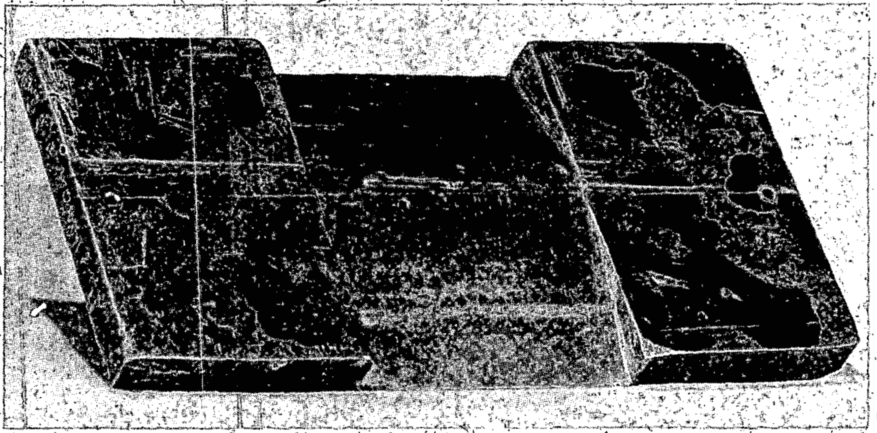


Fig. 9.20 — Hand-figured lead lens for rotating-source gamma chamber.

3.6 *Wall-mounting Gamma Monitor.*[17] A small a-c-powered gamma monitor designed for wall mounting was developed to monitor the gamma-radiation intensity in working areas. The monitor circuit is shown schematically in Fig. 9.22 (p. 234). A transformerless power supply and

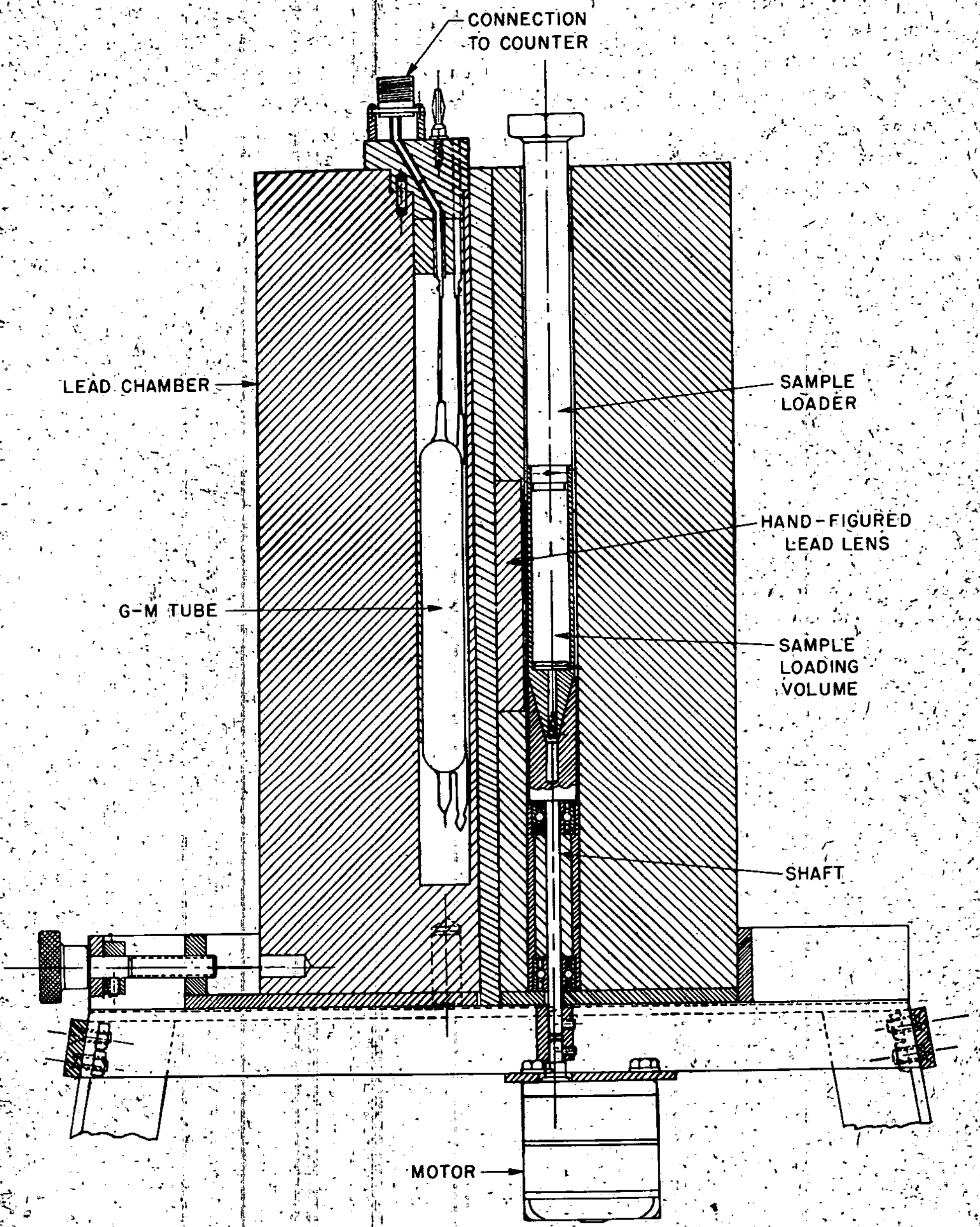


Fig. 9.21—Rotating-source gamma-chamber assembly.

series-connected vacuum-tube heaters are utilized. The high voltage for the Geiger tube is generated by a pulse power supply consisting of vacuum tubes V_5 and V_6, the inductor L, and a cold-cathode rectifier V_7. The high voltage is regulated by the corona discharge voltage regulator V_8.

This monitor was designed for ease of servicing, compactness, light weight, and stability. The over-all dimensions of this monitor are 10 by 8 by 3 in., and the total weight is slightly more than 7 lb. Figure 9.23 gives a rear view of the monitor showing the mounting holes, calibration access holes, and the protected accessible mounting of the Geiger tube.

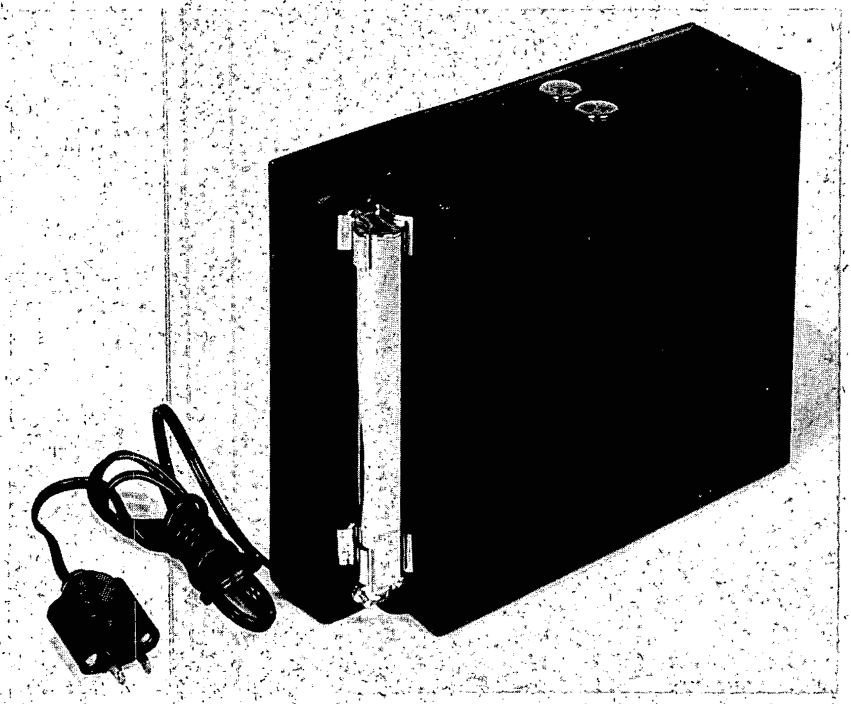


Fig. 9.23—Wall-mounting gamma monitor, rear view.

The gamma-radiation intensity that penetrates the Geiger tube is indicated by a panel meter on the front of the instrument. Full-scale deflection of this meter corresponds to 100 counts/sec.

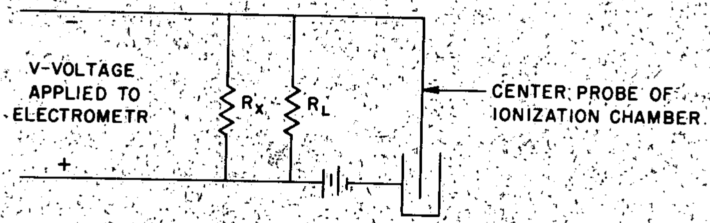
3.7 *Underwater Electrometer.* An immersible ionization chamber which is remote from its associated ion-current-indicating electrometer has been used at Mound Laboratory for the assay of irradiated bismuth slugs which are stored in a pool of water (Chap. 7, Sec. 3.3). This instrument was based on an Oak Ridge National Laboratory design. The ion current produced in the ionization chamber as a result of the gamma flux from an irradiated bismuth slug provides a measure of the polonium content of the slug being assayed.[18] The deflection of a Lindemann-Ryerson electrometer is calibrated to present a reading, on a ground-glass scale, which is proportional to the gamma flux impinging on the ionization chamber. Figure 9.24 shows a simplified circuit diagram of the underwater electrometer, and Fig. 9.25 shows the electrometer housing, the remote ionization chamber with a slug positioned in front for measurement, and the periscope used for identifying the slug being assayed.

4. SPECIAL PURPOSE INSTRUMENTATION

4.1 *General.* Special problems which were not primarily associated with the detection of radiation have occasionally originated in some phase of the polonium purification process. Representative solutions to the type of problem encountered are described in this section, and these include only that apparatus for which significant needs were satisfied or in which novel ideas were expressed.

4.2 *Quartz-fiber Microbalance (by James M. Goode).* (a) *General.* The determination of the purity of polonium preparations made it desirable to weigh a mass of polonium of the order of 40 μg with an accuracy of ±0.05 μg. Commercial microbalances were not suitable for this determination for two reasons: (1) the sensitivity of even the best available commercial microbalance was far too low to achieve the desired accuracy, and (2) the speed of these balances was low enough to allow sample deterioration due to prolonged atmospheric exposure. The quartz-fiber microbalance designed by Kirk, Craig, Gullberg, and Boyer[19] for plutonium analysis had the desired sensitivity and construction features to give the required accuracy and speed of operation. Balances of this type were being supplied to the Manhattan Project by the Ryerson Instrument Shop of the University of Chicago. An agreement was reached with the Ryerson Instrument Shop for the supply (and maintenance) of quartz-fiber microbalances to the Dayton Project.

A program was started at the Dayton Project in 1946 to modify the quartz-fiber microbalance and adapt it to the specialized needs of this Project. Provision of facilities for on-site maintenance of existing microbalances was started in 1947. The fabrication of modified quartz-fiber microbalances began in 1948.



CIRCUIT DIAGRAM INVOLVING THE IONIZATION CHAMBER

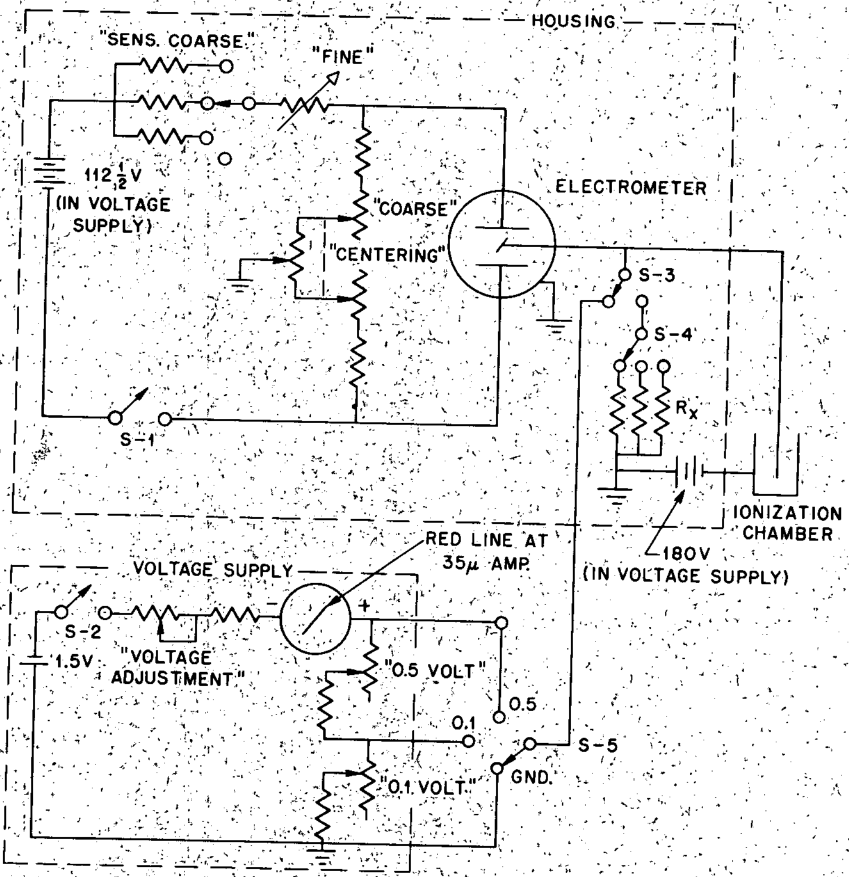


Fig. 9.24—Underwater electrometer, simplified schematic.

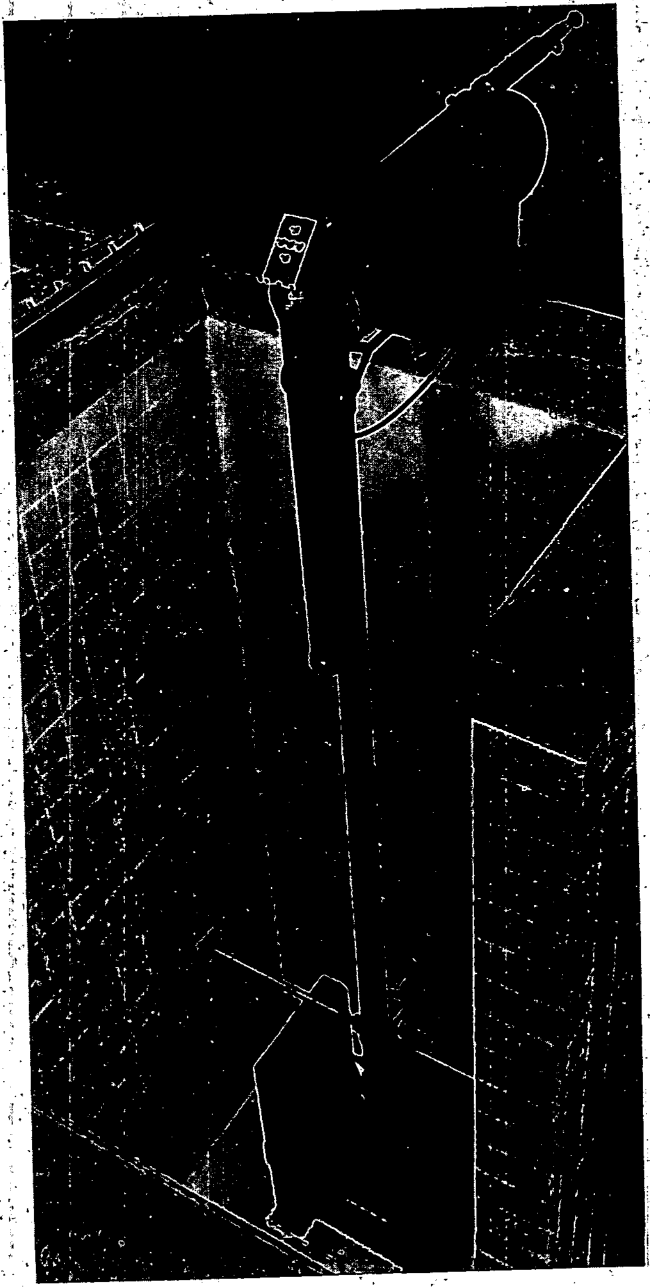


Fig. 9.25 — Underwater electrometer installation.

(b) *Microbalance Construction.* The Mound Laboratory balance is an adaptation of the quartz-fiber balance (referred to as the Kirk-Craig balance) which is constructed by Kirk, Craig, Gullberg, and Boyer.[19]

The Kirk-Craig balance consists of a fused-quartz equal-arm beam suspended by two identical quartz fibers. One of these fibers is used as a torsion fiber for restoring balance when an unbalanced force is applied to the pans. The other fiber is used as a support. Since this is a null-type balance, the support fiber does not enter into the calibration of the balance. Tension on the torsion and support fibers is maintained by a stretched quartz bow. The balance pans are suspended from the beam by small hinge (or hang-down) fibers fused directly to the beam. These hinge fibers are fused to heavier fibers which are hooked at the ends to hold the pan holders. The pan holders are located in a well beneath the main-balance-case bottom in order to isolate the sample and tare microfoils from the major portion of the balance.

The null point of the system is indicated by comparison of projected images of an index fiber stretched across the top of the beam. The quartz system and the optical system are encased within an inner shield, and the entire mechanism is contained within an outer case.

During 1943 the construction of these balances was undertaken by the Ryerson Instrument Shop at the University of Chicago under the direction of T. J. O'Donnell. Certain modifications to the original Kirk-Craig balance were made at this time. In addition to the original shields, a thick plastic case for atmospheric and thermal shielding was provided. A control base for ease of remote operation was also added. The torsion dial drive was improved, and the optical system was modified.

The Dayton Project used balances constructed by the Ryerson Instrument Shop for routine weighing in the determination of the purity of polonium from 1944 to 1948. In 1947 the relative scarcity of microbalances led to the initiation of a program for maintenance of quartz-fiber microbalances at the Dayton Project. A program of balance repair and construction was initiated, and by September 1948 a balance constructed entirely at the Dayton Project had been completed.[20]

The quartz system of the balances constructed at Mound Laboratory is basically the same as that designed by Kirk, Craig, Gullberg, and Boyer.[21] The balance case, optical system, and mechanical system were modified to make the balance easier to operate and more dependable. Because of the particular nature of the radioactive material being weighed (polonium in this case), a loading mechanism combining atmospheric isolation and completely remote pan-loading were incorporated in a new vacuumtight balance case of cast metal. A motorized drive was added to the torsion-fiber dial to increase the speed of weighing. With these modifications, an experienced operator can average 12 weight determinations per hour. In addition to increasing the speed of operation, the modifications greatly extended the period of trouble-free operation. Some of the Mound Laboratory balances have been in routine service for over a year without failure or service on any part of the balance.

A schematic drawing of the quartz system and the optical system is shown in Fig. 9.26, and a pictorial representation is shown in Fig. 9.27. A front view of a Mound Laboratory balance with its associated accessories is shown in Fig. 9.28. The pan-well interior is seen in both a profile and an oblique view, simultaneously, through a telescope. A typical view as seen through this telescope is shown in Fig. 9.29. The light for viewing the pan wells is transmitted through two thicknesses of heat-absorbing glass (Corning Light Shade Aklo No. 3965). This glass, which is used also in the light path of the index lamps, reduces the thermal drifts (due to convection and to unequal heating of the quartz system) to a negligible amount after 5 min of operation.

A porous container of desiccant (Drierite) is placed inside the outer balance case. The inclusion of the desiccant and the complete shielding of the balance from the atmosphere have eliminated the need for drift correction and have greatly extended the useful life of the rhodium first-surface mirrors, the quartz system, and other functional parts within the balance case.

Rotation of the torsion fiber of the Mound Laboratory quartz-fiber balance is arbitrarily limited to three complete revolutions, in either direction, from the center position. The torsion-fiber dial, which is 5 in. in diameter, is divided into 1000 divisions and is equipped with a vernier reading to $^1/_{20}$ of a division. The dial is motor driven through a 200-to-1 reduction worm drive. A motor with a double shaft extension is used. One shaft extension is equipped with a handwheel for fine adjustment of the torsion-fiber dial.

The null position is determined by aligning the projected images of the two ends of the index fiber on a ground-glass screen. The resolution of the optical system is sufficient to detect a displacement of position corresponding to $^1/_{10}$ diameter of the 10- to 15-μ index fiber. The beam index sensitivity (defined below) is adjusted so that a displacement of $^1/_{10}$ of the index fiber is roughly equivalent to $^1/_{20}$ of a dial division (one vernier division).

The sensitivity of the balance is determined by two factors, the beam index sensitivity and the torsion constant. The beam index sensitivity is a function of the physical and geometrical properties of the quartz-fiber assembly and optical system and is defined as the angular displacement of the beam per unit of unbalancing force applied to the pans.

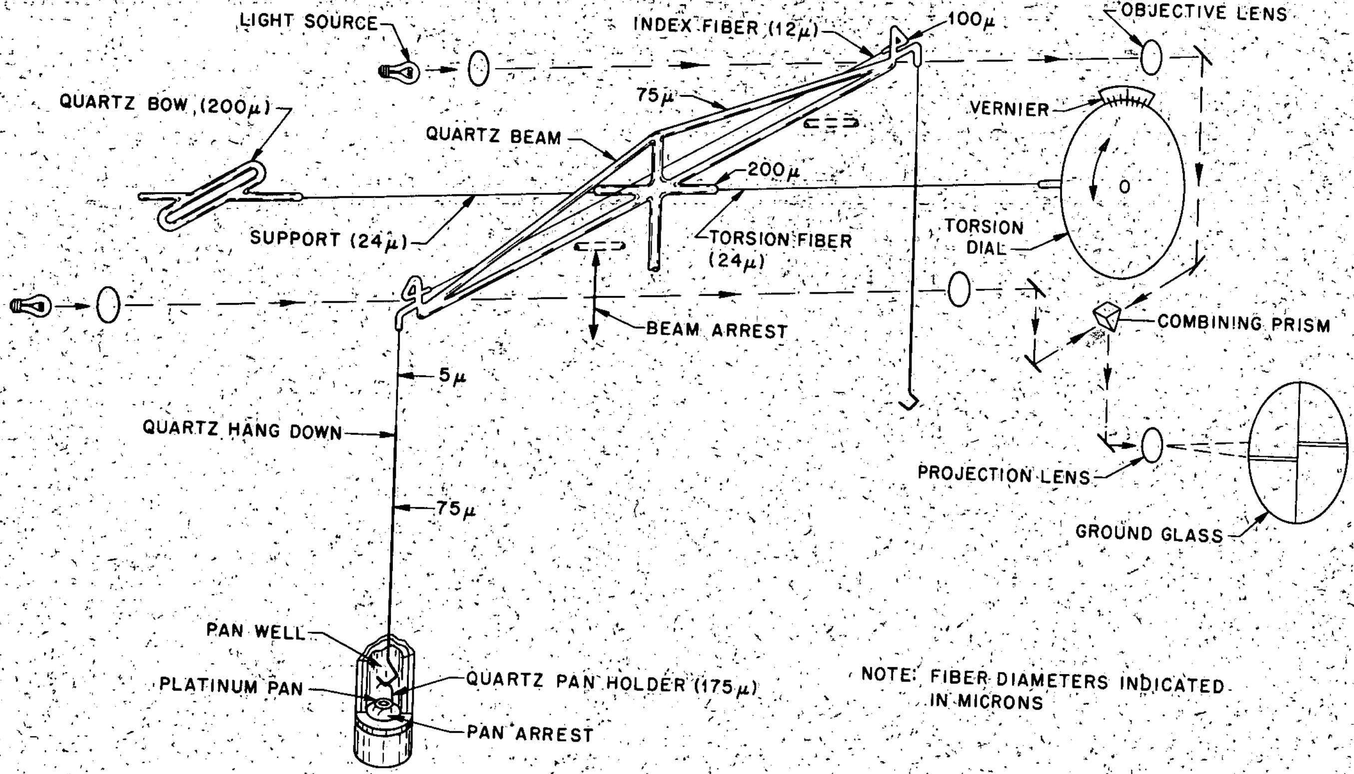
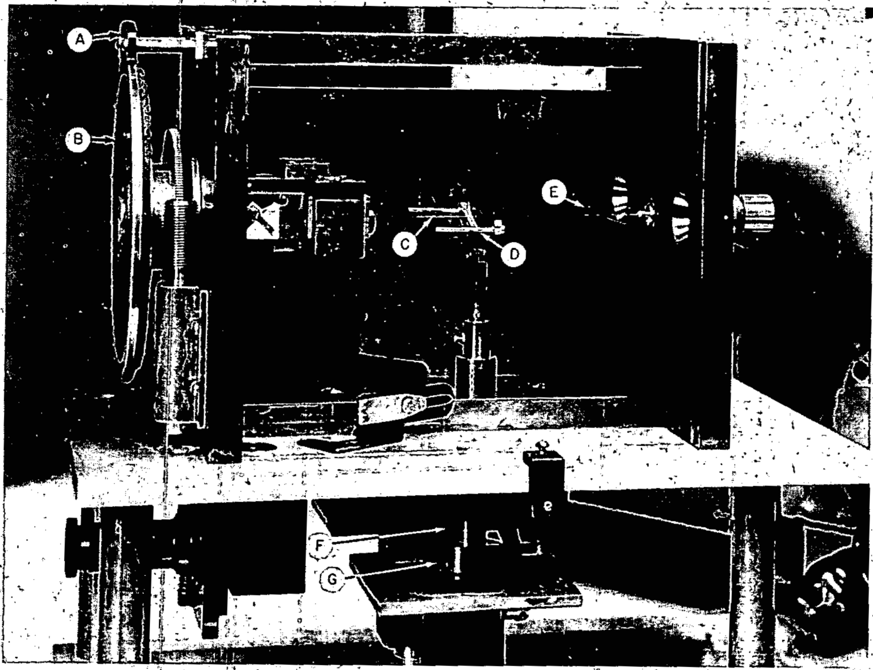


Fig. 9.26—Quartz system and optical system, schematic.

This may be expressed in terms of degrees per microgram. The beam index sensitivity is adjusted by shifting the position of the center of gravity of the beam. The torsion constant is a function of the torsion-fiber dimensions and beam length. It is defined as the mass which, when placed on one pan, will cause a displacement such that it will

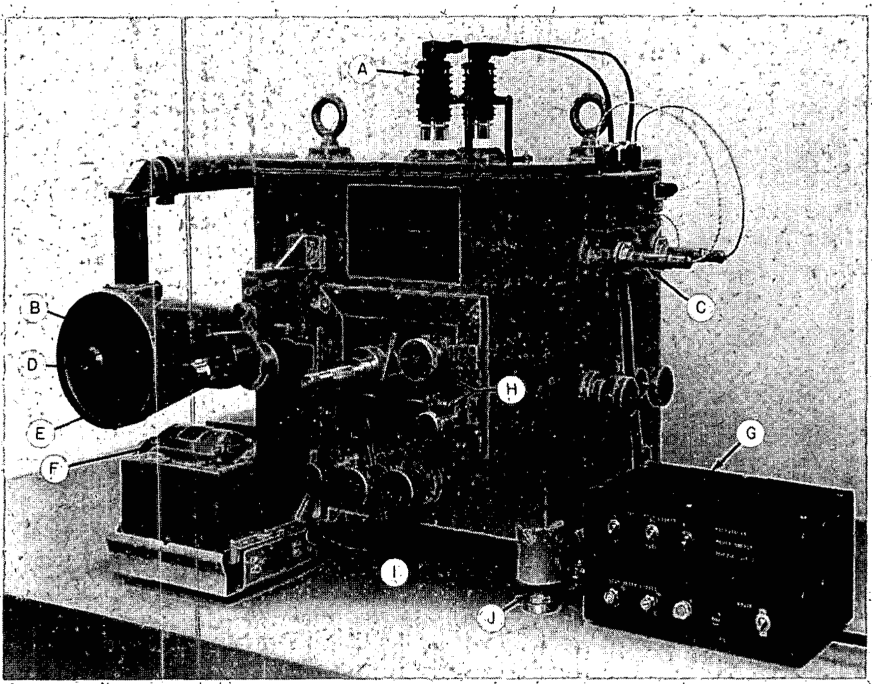


A. Torsion-fiber dial vernier
B. Torsion-fiber dial
C. Quartz beam
D. Beam arrest
E. Quartz tension bow
F. Pan well
G. Pan arrest

Fig. 9.27 — View of microbalance quartz system.

require a movement of one dial division of the torsion-fiber dial to return the system to the null position. The torsion constant is expressed in terms of micrograms per dial division and is varied by selection of a torsion fiber of appropriate diameter. The range of the torsion constants of the balances in use at Mound Laboratory is between 0.20 and 0.25 μg per dial division.

The Mound Laboratory balance is normally used with an 8- or 9-mg load per pan. The balance is rated at a load of 20 mg per pan. Above the rated load, sagging of the beam due to stretching of the tension bow carries the index fiber out of view of the optical system. No serious attempt has been made to extend the load range or even determine the maximum load of the balance, since, for routine weighing, the balance is used at a loading of less than $\frac{1}{2}$ of the rated load.



A. Pan-well lights
B. Ground-glass screen
C. Beam index fiber lights
D. Vernier scale and beam index eyepiece
E. Telescope
F. Dial drive motor
G. Power supply
H. Micromanipulator controls
I. Sealed sample carrier
J. Leveling screws

Fig. 9.28—Quartz-fiber microbalance, front view.

The accuracy of the Mound Laboratory balance is dependent upon the accuracy of the weights used to calibrate the torsion constant of the torsion fibers. In 1948 a set of eight small platinum microfoils weighing between 7 and 9 mg was prepared at Mound Laboratory, and their weights were determined by the National Bureau of Standards. The weight of individual microfoils in the set was certified to be within 0.2 μg. The microfoils were recalibrated by the Bureau in 1951.

The torsion constant of a balance is determined by observing the twist of the torsion fiber necessary to restore the beam to null position upon application of a known weight difference to the pans of the balance. The torsion constant is determined over a range of 6000 dial divisions (six complete turns) or an equivalent of 1.2 to 1.5 mg.

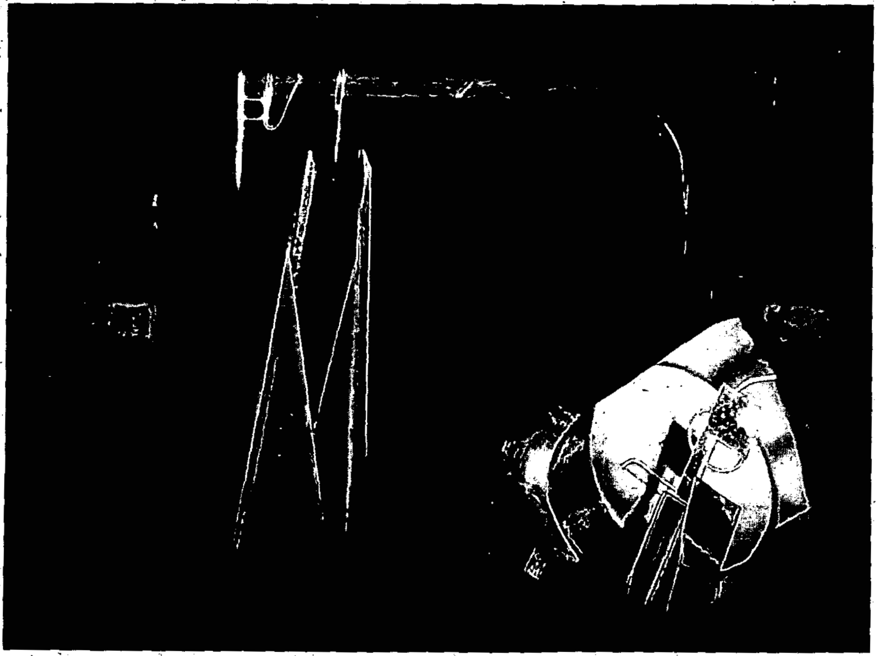


Fig. 9.29 — Pan-well interior as seen through telescope.

The calibration error can be reduced to 0.11 μg in a range of 1 mg by utilizing only the differences in the full set of certified weights. The normal weight of the sample of polonium weighed for purity determination is 40 μg. The error in the sample weight due to calibration error is, then, 0.004 μg.

The weight of the polonium sample, in practice, is determined to only the nearest 0.1 μg. A greater accuracy of weight determination would be meaningless for routine operation because the accuracy of the counting methods used to determine the radioactive component of the sample is of the order of 1 per cent. The "weight" of a given microfoil is measured twice to determine the quantity of polonium plated. Weight is used in a restricted sense here because the absolute weight of the microfoil is not determined, but rather its weight with respect to another (tare) microfoil. After the polonium has been plated on the microfoil, the weight is determined again in comparison to the same tare microfoil. Although the absolute weight of this microfoil is not determined accurately, the difference in weight, before and after plating, is determined quite accurately from the known torsion constant of the balance.

The heat from a polonium-plated microfoil is sufficient to cause an error in weighing (if the weighing is done in air) due to what is termed the "buoyancy" effect. An investigation of this effect was made,[22] and a correction for it was determined. This correction is routinely applied to each purity determination.

The operation of the balance is relatively simple. The sample to be weighed is inserted into the balance by a microfoil holder in conjunction with a mounting block (Sec. 4.6). A micromanipulator is built into the side of the balance case to provide linear motion to the mounting block in the plane of the balance-case side. A horizontal motion at right angles to the balance-case side and a rotary motion are provided by the foil holder. The sample is mounted on the pan holder of the balance by means of these manipulations. A rotary motion can be imparted to the pan holder by the pan arrest to orient the pan holder for receiving or removing a sample. The operation of the foil holder in the pan well can be viewed in a profile and in an oblique view through the telescope provided (Fig. 9.29). The null position of the balance is approached rapidly by the motorized drive on the torsion-fiber dial. Final adjustment of the torsion-fiber dial is made by manual adjustment through an extension of the dial drive-motor shaft. Because the torsion constant is set at 0.20 to 0.25 μg per dial division and the rotation of the dial is limited to three full turns each side of center, the limit for weighing, without change of tare weight, is the tare weight ±600 to 750 μg.

(c) *Quartz-fiber-drawing Apparatus.* The construction of quartz-fiber instruments in quantity or to close performance specifications is dependent upon the availability of an adequate supply of fibers of the desired size and quality. Various methods of drawing quartz fibers have been described[23–27] in which the diameter of fibers drawn can be predicted only within wide limits of error. Continuous fiber-drawing methods[28–30] will permit observation and adjustment of fiber diameter during the course of the draw, and it is this type of apparatus which was developed[31,32] at Mound Laboratory to provide necessary fibers for the quartz-fiber microbalance.

The method of fiber drawing described hereafter is an extension of the Kirk-Schaffer[28] and O'Donnell[29] reel-drawing methods. A major improvement in the method of fiber drawing has resulted from the establishment of the concept of constant-efficiency conversion of quartz cane to fiber at a steady rate as a basic requirement for drawing uniform-diameter fibers.[33] It can be shown[31] that for steady-state conditions the diameter of fiber drawn is determined by the following relation:

$$V_f = V_c \left(\frac{D_c}{D_f}\right)^2$$

where V is the velocity, D is the diameter, and f and c refer to fiber and cane, respectively. It is seen that the control of drawn-fiber size is most easily accomplished through adjustment of the ratio of cane velocity to fiber velocity.

The drawing equipment incorporates facilities for adjustment and control of factors affecting the draw. The equipment was designed and built in units, each having a wide range of operating conditions, in order that diameter-reduction ratios, heating conditions, etc., could be varied independently. The equipment is shown in Fig. 9.30. The feed rate on the cane-feeding unit is continuously variable from 0.00 to 2.00 in./min. The fiber-reeling unit draws the fiber axially from the cane onto the reel, and a motorized transmission and speed indicator provide control and indication of reeling velocities up to 10,000 in./min. The fusion control unit includes a heat source, an inclined-eyepiece binocular microscope for observation of the fiber fusion area, and adjustable torch and microscope supports having both coarse and fine movement controls.

The equipment developed at Mound Laboratory has been used with bulbous-type slightly oxidizing oxypropane flames to draw and reel up to 150-ft lengths of quartz fibers from 0.00008 to 0.016 in. in diameter and to draw 3-ft lengths of fibers up to 0.040 in. in diameter.[31]

4.3 *Polarograph.* Conventional methods of investigating the electrochemical properties of materials with high specific radioactivities are limited by the interference of decomposition products produced by irradiation of the solvent. A polarograph, which is based on a method described by Joliot,[34] has been used at Mound Laboratory to study the deposition of polonium from hydrochloric acid solutions. In this method the deposition of polonium is detected (without interference caused by inactive decomposition products) by continuously recording the alpha-induced ionization current in the vicinity of an alpha-transparent electrode. A schematic representation of the polarograph which was devised at Mound Laboratory is shown in Fig. 9.31.

In the discussion which follows it is assumed that polonium is deposited on the cathode (or negative electrode); however, it should not

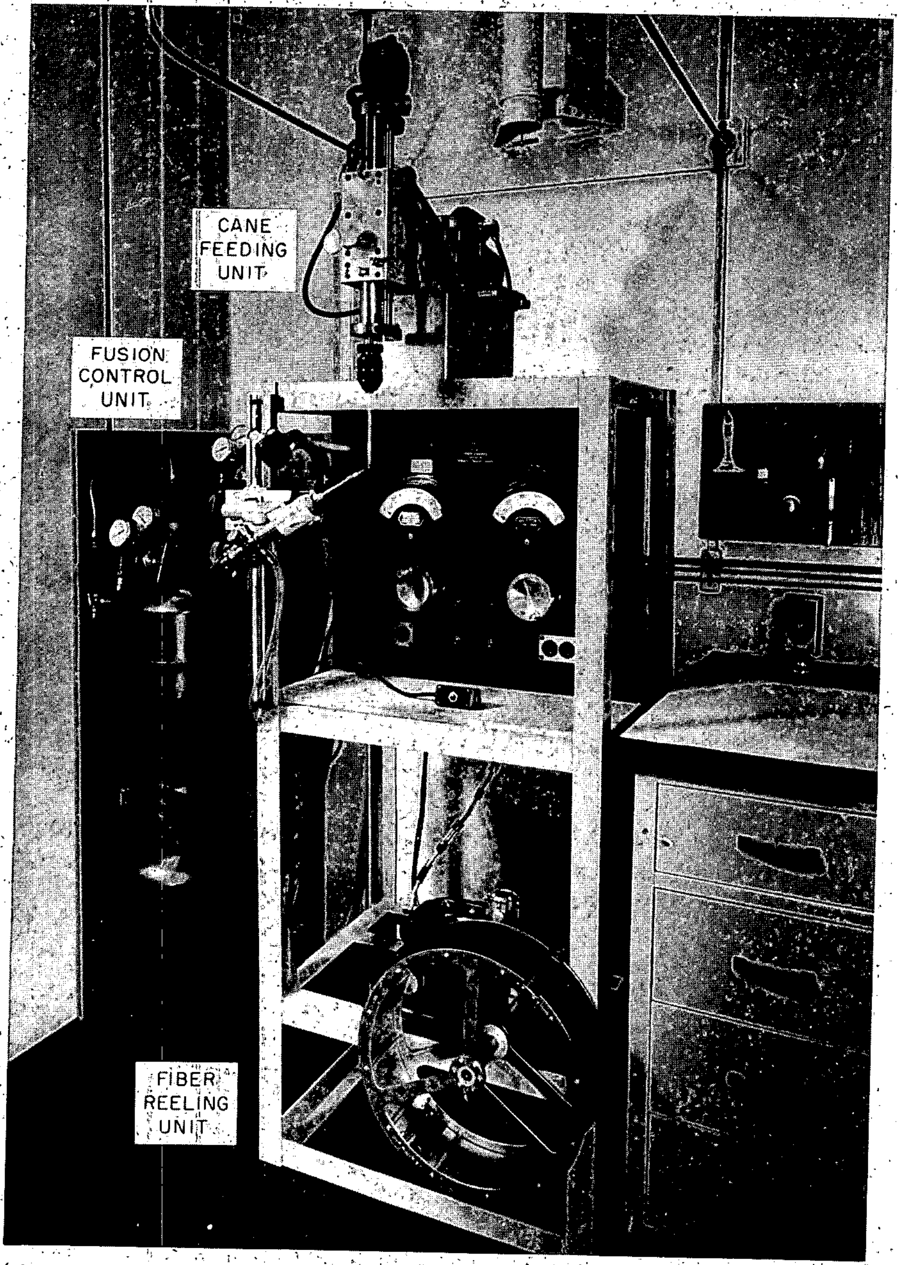


Fig. 9.30—Quartz-fiber-drawing apparatus.

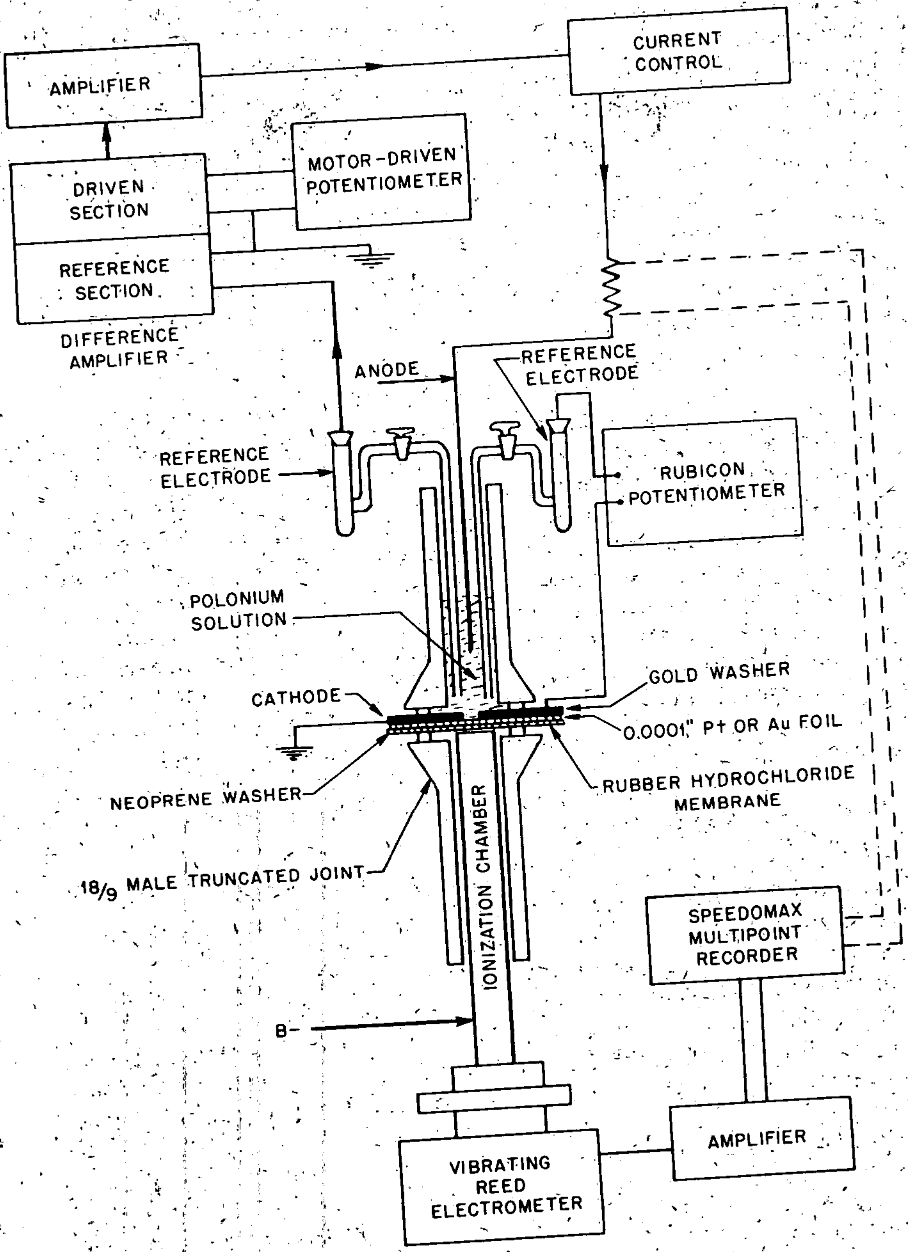


Fig. 9.31—Mound Laboratory polarograph.

be inferred that deposition onto the anode never occurs in practice. Either electrode can be the recipient of the electrodeposited polonium, but clarity considerations necessarily restrict the discussion to one electrode, in this case the cathode.

The concentration of polonium on the cathode is followed by measuring the current from an ionization chamber placed adjacent to the radiation-transparent electrode.[35] The Mound Laboratory polarograph permits the electrode potential to be uniformly varied while the ionization current in the vicinity of the cathode is continuously recorded on a Speedomax (Leeds & Northrup Company) recorder. Inflections in the ionization current-potential relation occur as the element passes through various oxidation states.

The cathode (foil) potential relative to that of a reference half-cell is controlled by varying the grid potential of one stage of a difference amplifier by means of a motor-driven slide wire.[36, 37] This potential is uniformly varied toward either a more positive or more negative value. The driving gears to the motor-driven slide wire are so arranged that rapid changes in the direction of motion of the slide wire can be made. In those cases where anode control (rather than cathode control) is desired, a phase inverter is added between the amplifier and current control circuits, and all other circuit parameters remain unchanged. The dissimilarity of cell-current and ionization-current behavior during a cathodic sweep (range of potential variation) of a polonium solution in hydrochloric acid is shown in Fig. 9.32. Oxygen and hydrogen reduction, as well as increased concentrations of reducible products at the cathode surface after the reduction of polonium, causes the inflection points in this curve.

4.4 *Electronic Plating Control.* The Mound Laboratory Models PC-4 and PC-5 four-unit plating controls are electronic instruments which control four simultaneous electroplating processes.[38] They maintain the solution-cathode potential of each plating cell constant over a wide range of ionic concentrations of the solution.

These instruments evolved from a battery-powered plating-cell control circuit designed at the Los Alamos Scientific Laboratory[39] to control the selective plating of one metal from a solution of two or more metals.

A schematic diagram of the Model PC-5 plating-control circuit is shown in Fig. 9.33. This diagram is typical of both models; they differ from each other chiefly in the type and number of output tubes. A simplified schematic diagram of the control circuit and plating cell is shown in Fig. 9.34.

The control circuit consists of a difference amplifier (V-1 and V-2), resistance coupled to a pentode amplifier (V-3), which controls the degree of conduction of the output stage (V-4). The plating cell is the cathode load of V-4; therefore the plating current is the plate current of V-4.

In operation the plating current is adjusted to the value that gives the desired solution-cathode potential as indicated by the vacuum-tube voltmeter. This is done by adjusting the bias applied to the grid of V-2 and then making a fine adjustment by varying the cathode resistance common to V-1 and V-2. Thereafter any change in solution-cathode potential will appear as an error signal at the grid of V-1 which will result in a corrective change in the degree of conduction of V-4 to maintain the desired solution-cathode potential. The error signal is the algebraic sum of the solution-cathode potential and the reference half-cell potential.

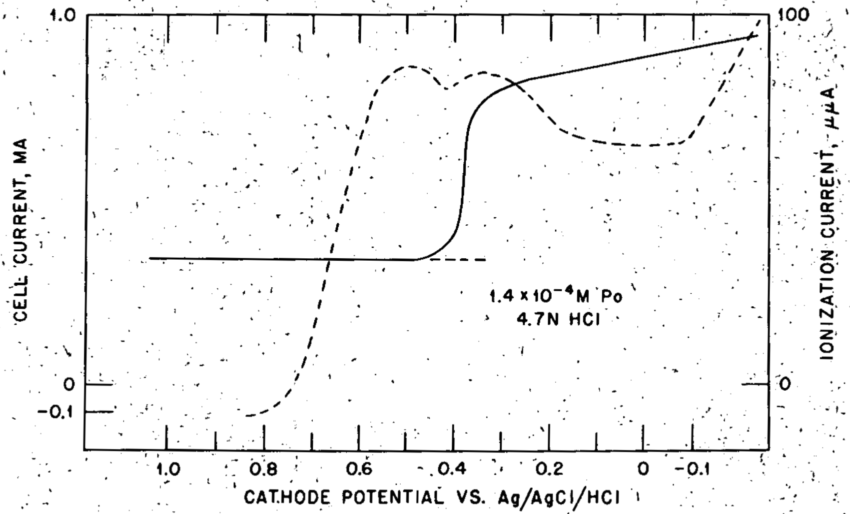


Fig. 9.32—Dissimilarity of cell-current and ionization-current behavior. -----, cell current; ——, ionization current.

The control circuit is highly degenerative due to the feedback loop which includes the plating cell and the calomel reference half-cell and also the feedback loops from the plate of V-3 to the cathode of V-2 and the grid of V-3. The voltage gain from the grid of V-1 to the grid of V-4 with feedback is approximately 280. The voltage gain without feedback is greater than 10,000.

The plating control normally maintains the solution-cathode potential to within ± 10 mv (see reference 40) of the initial value during the plating operation, which may require several hours for essentially com-

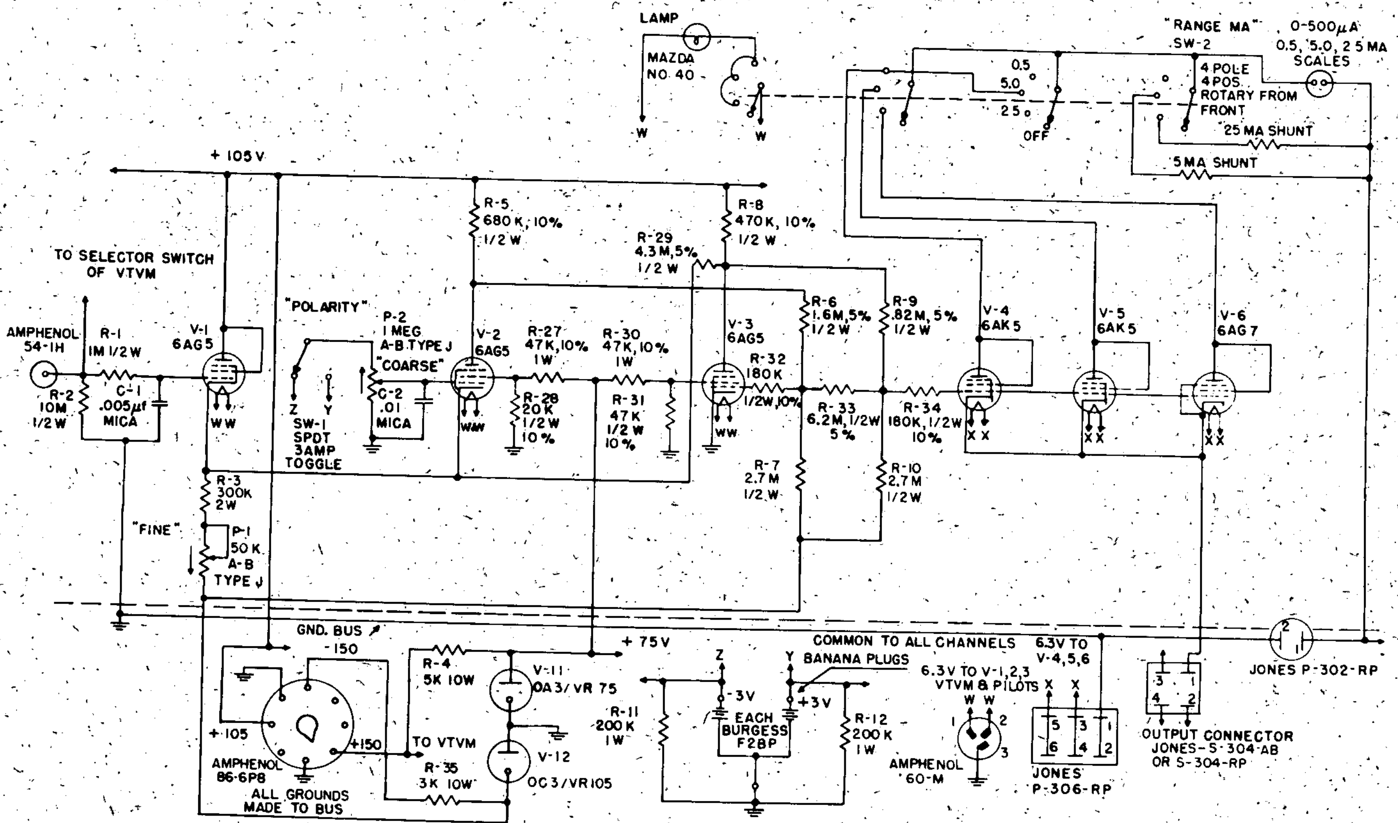
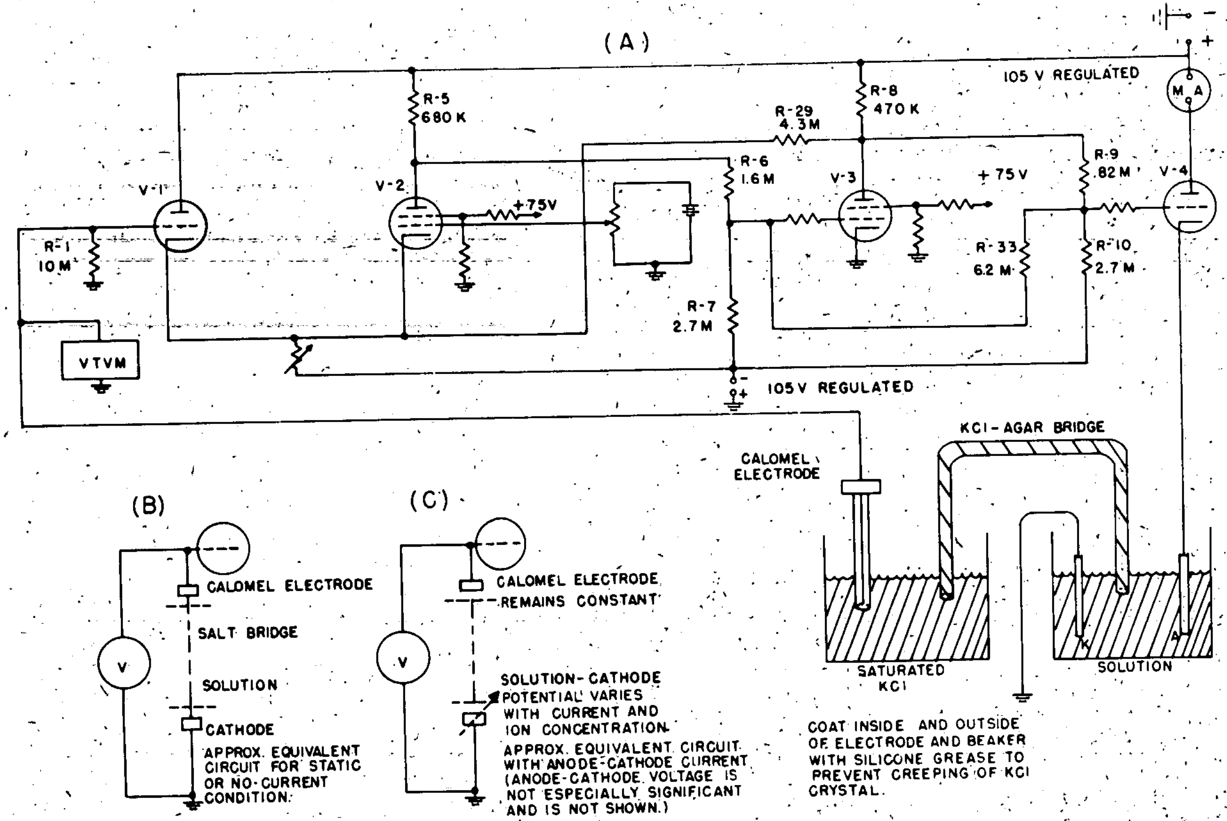


Fig. 9.33 — Model PC-5 plating control.



APPROX. EQUIVALENT CIRCUIT FOR STATIC OR NO-CURRENT CONDITION.

APPROX. EQUIVALENT CIRCUIT WITH ANODE-CATHODE CURRENT (ANODE-CATHODE VOLTAGE IS NOT ESPECIALLY SIGNIFICANT AND IS NOT SHOWN.)

COAT INSIDE AND OUTSIDE OF ELECTRODE AND BEAKER WITH SILICONE GREASE TO PREVENT CREEPING OF KCl CRYSTAL.

Fig. 9.34—Simplified schematic of control circuit and plating cell.

plete deposition. This is true so long as the control is operated within its current rating, even when operated in parallel with a manual control. Control within ±2 mv is not uncommon. Three plating-current ranges are provided. They are selected by means of a rotary switch which also selects the appropriate shunt for the plating-circuit milliammeter.

The vacuum-tube voltmeter, Fig. 9.35, used for measuring the solution-cathode potential is a degenerative cathode-loaded circuit devised by Bradley.[41] This circuit has been found to be quite stable. Grid-current effects are negligible under all operating conditions, and tube selection is not required.

The Model PC-4 and PC-5 plating controls require two power supplies for their operation. One power supply furnished +150 volts d-c, −150 volts d-c, two individually adjustable 25-volt taps for the vacuum-tube voltmeter, and +105 volts d-c for the plating-control direct-coupled amplifier (excluding the plating circuits). The 25-volt taps are unused in some models of the plating control. A second power supply furnishes +105 volts d-c for the plating circuits. The 150-volt power supply is shown schematically in Fig. 9.36.

The two power supplies are electrically similar and employ regulating circuits of a type described by Abate.[42] In these circuits both the output voltage and the total current drawn from the power supply are electronically regulated.

The +150-volt output is regulated by means of a conventional degenerative regulating circuit consisting of a series regulator tube, V-6 (Fig. 9.36); a control tube, V-1; a voltage reference tube, V-7; and grid-coupling tube, V-5. The purpose of V-5 is to increase the amplitude of the error signal applied to the grid of V-1.

The −150-volt output is regulated by means of the network consisting of tubes V-9 and V-10, control amplifier V-4, voltage reference tube V-8, and grid coupling tube V-3. The control signal for this network is obtained from the voltage developed across R-22 in parallel with the network consisting of R-16, R-17, and P-2.

In addition to regulating the −150-volt output, this network improves the regulation of the positive output section of the power supply by presenting a constant load to the power transformer, rectifier, and filter network. This is true since V-9 and V-10 are shunted across the positive output section of the power supply and constitute a ballast, which maintains the load current constant at the output of the power-supply filter network, by maintaining a constant potential across R-22 through which essentially all of the load current flows. Another effect of this network is to give the power supply a smooth overload characteristic. As soon as the output current exceeds the maximum current which V-9 and V-10 will conduct when the power supply is unloaded, V-9 and V-10 cease conduction and the internal impedance of the power supply be-

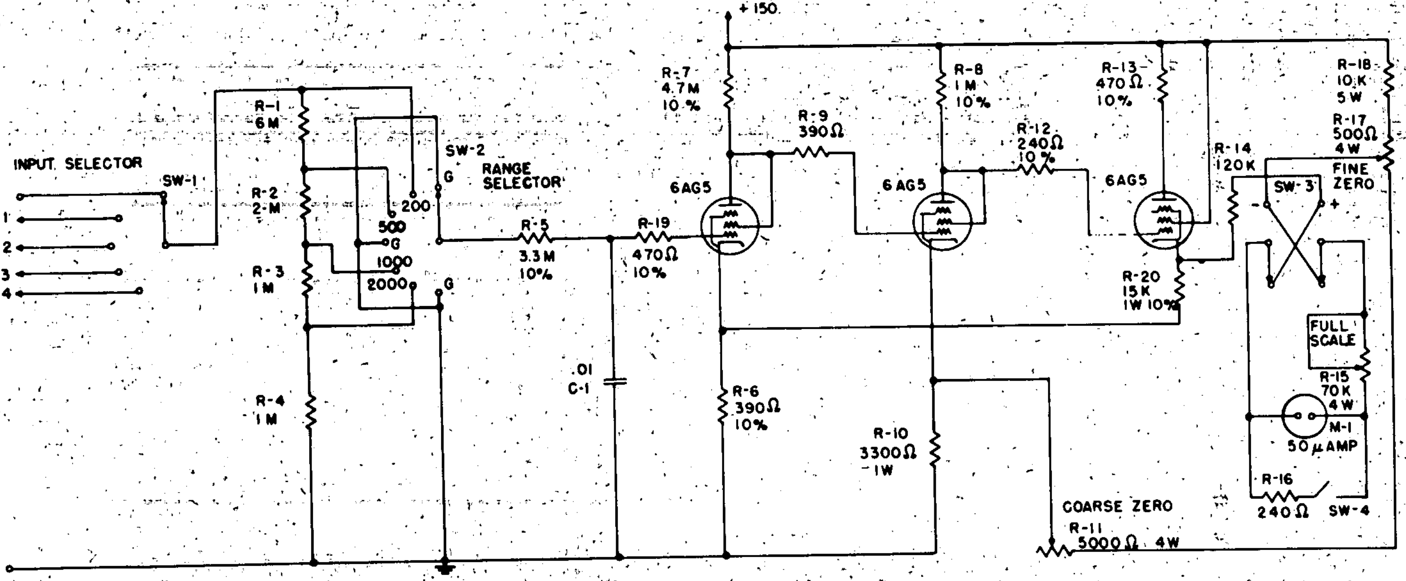


Fig. 9.35—Vacuum-tube voltmeter.

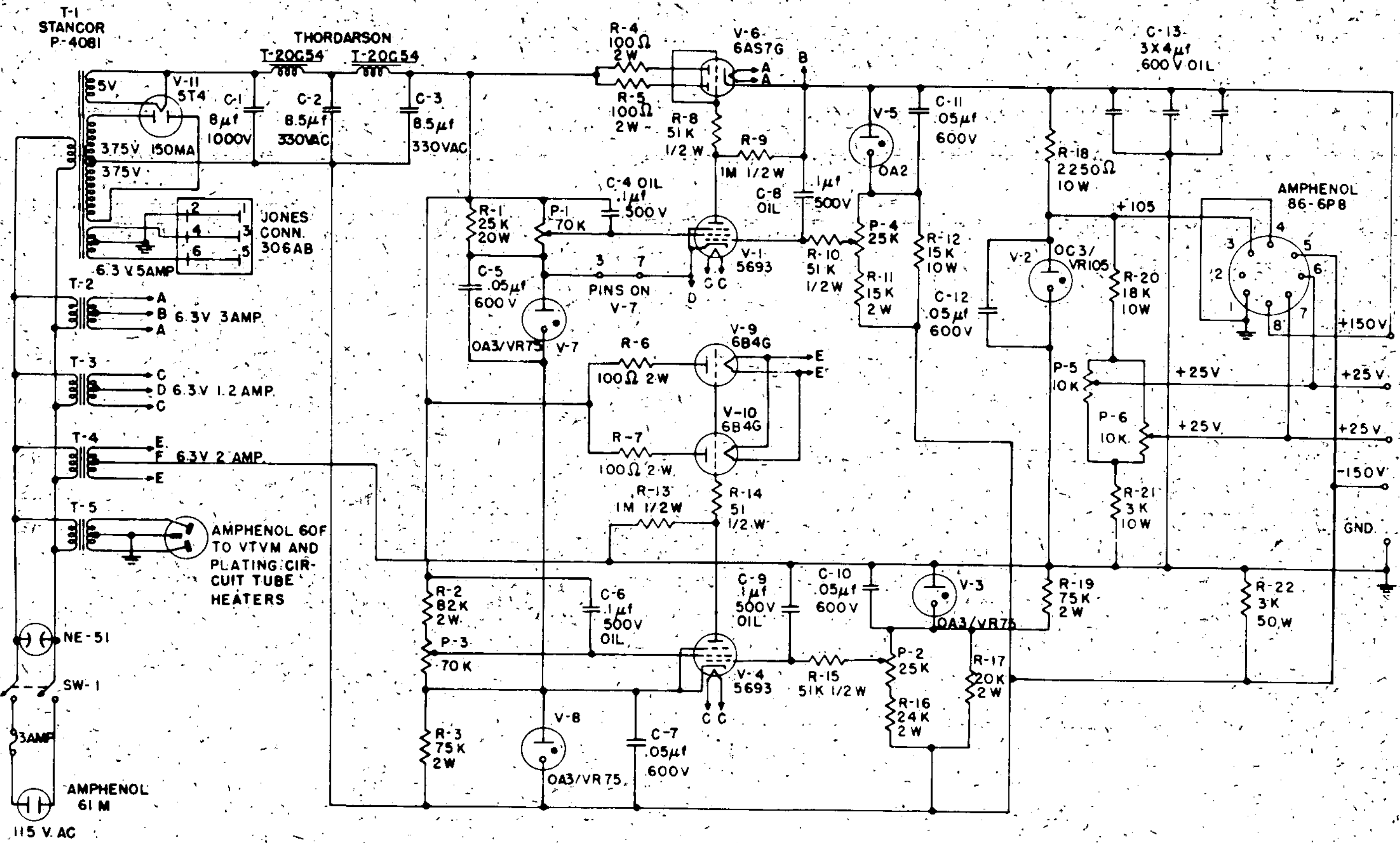


Fig. 9.36—150-volt power supply.

comes essentially equal to R-22. For output currents below this maximum, the internal impedance is equal to the low dynamic impedance, which prevails with current regulation. The power supply is thus protected from short circuits, and the external load current may be limited to a safe value by choosing a suitable value for R-22.

The power supply is adjusted for best regulation by connecting a dummy load equal to the rated load to the output jacks, with provision for switching the load in and out of the circuit. After a 30-min warm-up the screen- and control-grid voltages of control tubes V-1 and V-4 are alternately adjusted to obtain best regulation at rated output voltage, as determined with a differential voltmeter.

4.5 *A Low-power Induction Heater.* A schematic diagram of a low-power induction heater[43,44] designed to heat small metal objects to a temperature of about 150°C in 5 to 10 min is shown in Fig. 9.37. This instrument has been used extensively for moderate-temperature heating applications in the polonium process.

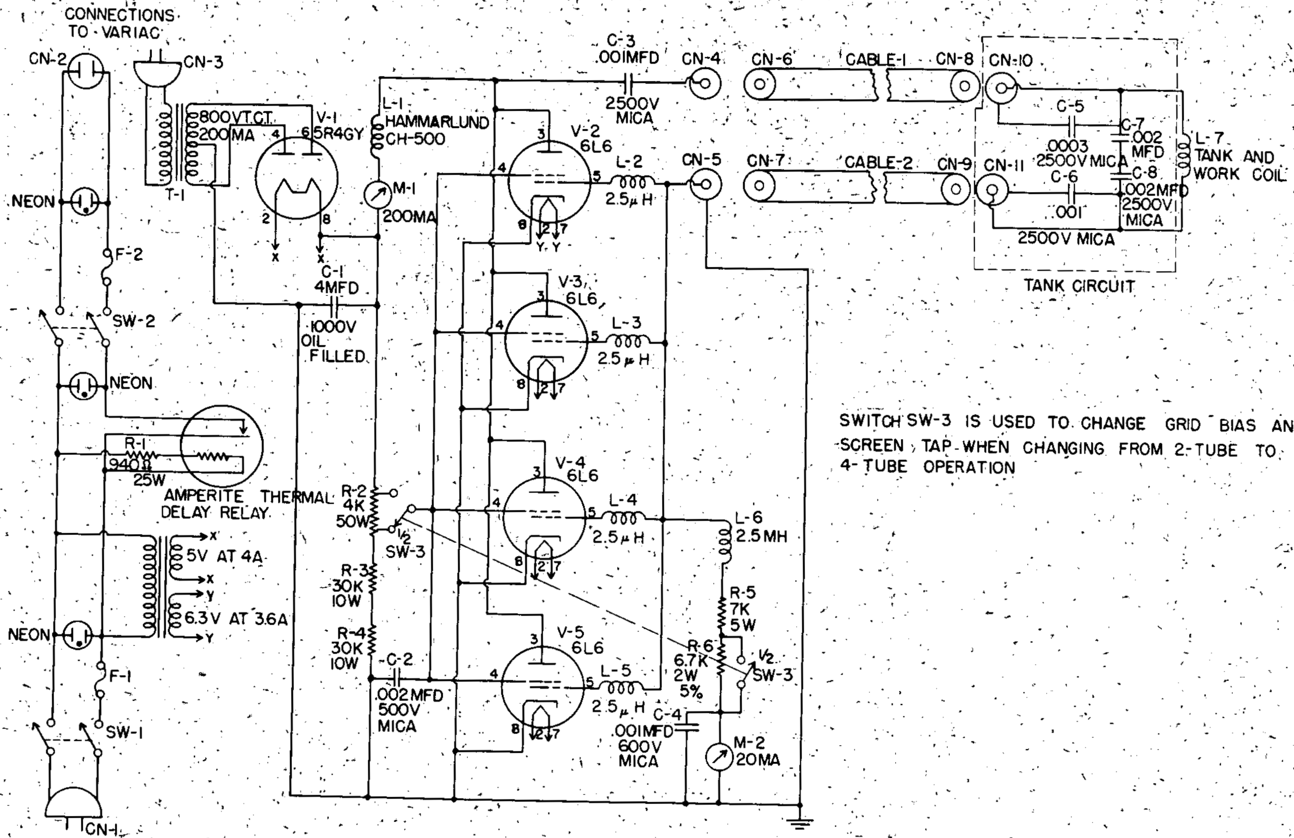
An operating frequency of approximately 3 Mc/sec was chosen so that the heater would be above the critical frequency of small platinum crucibles having 0.01-in.-thick walls. The critical frequency is defined by Brown[45] as the frequency for which the material thickness is equal to 2.25 times the skin thickness, where skin thickness is a measure of the degree of penetration of an alternating current below the surface of a conductor.

The heater is designed to operate with the tank circuit located 10 or 12 ft from the heater with the tank coil serving as the work coil.

The heater consists of a pair of 6L6 tubes connected in parallel in a Colpitts oscillator circuit. It was initially designed to utilize four 6L6 tubes in parallel. However, no appreciable increase in power output (due to power-supply limitations) was obtained by using four output tubes instead of two; the four-tube circuit is more disposed to parasitic oscillation.

The heater will deliver approximately 20 watts (using two tubes) through 12-ft lengths of coaxial cable to a nickel load consisting of a capped cylinder 0.66 in. in diameter and length with a weight of approximately 17 g. The highest temperature reached was 300°C. The 20-watt output represents a plate-circuit efficiency of about 33 per cent.

4.6 *Microfoil Holder (by C. E. Shoemaker).* One of the developments which made micro-purity assay possible on an accurate and rapid scale (Chap. 7, Sec. 11.2) was the successful design and construction of a microfoil holder which provided for the transfer of the polonium-plated microfoil from one piece of apparatus to another in a low-risk area. The holder is illustrated in Fig. 9.38, which shows one holder completely closed and another holder which has the foil extended. The ra-



SWITCH SW-3 IS USED TO CHANGE GRID BIAS AND SCREEN TAP WHEN CHANGING FROM 2-TUBE TO 4-TUBE OPERATION

Fig. 9.37 — Low-power induction heater.

dioactivity of the foil requires that it be kept in a high-risk area; thus a sealed barrier has to be provided between the inner chamber and the exterior of the foil holder. No part which is exposed to the high-risk inner chamber may pass through a barrier into a low-risk area. The holder fits three different pieces of apparatus and performs specific operations.

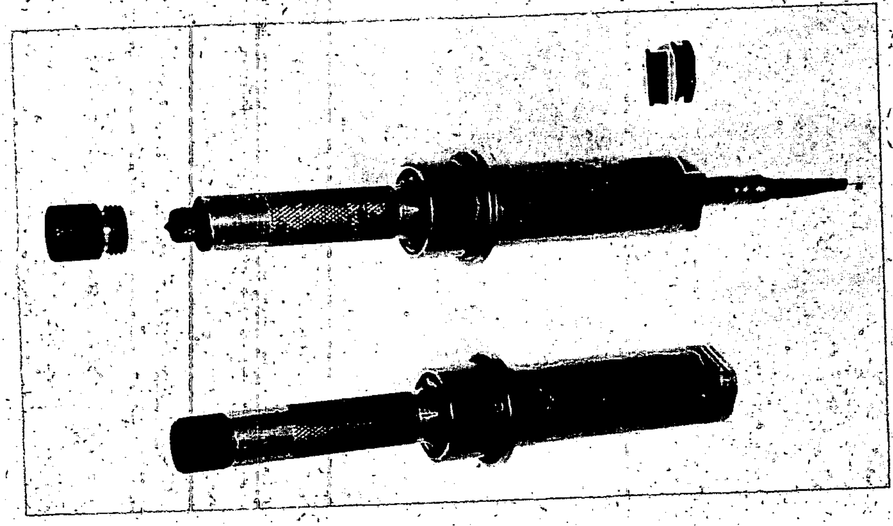


Fig. 9.38—Microfoil holders.

While the foil is being plated, it has to extend down into a small beaker. After being plated, washed, and rinsed, the foil is retracted into the holder which is evacuated, flushed, and sealed with helium at an absolute pressure of 5 in. Hg.

When the foil holder is used in the microbalance (Sec. 4.2), the foil must be extended in a horizontal position to be placed on the microbalance pan.

For counting in a Logac-L (Sec. 3.1) the foil must be placed in an evacuated atmosphere in a vertical position which is accurately located. Since each side of the foil is counted, it must be turned over. It must not move vertically or horizontally.

An integral associate of the foil holder is the mounting block in which the holder is mounted for the various operations and which moves the end plate of the holder to expose the inner chamber. Each piece of apparatus dealing with microfoils is equipped with one or more mounting blocks.

Figures 9.39 and 9.40 show a foil holder mounted in a sectioned mounting block. In Fig. 9.39 the end plate of the foil holder has been moved a sufficient distance to partially expose the inner chamber; in Fig. 9.40 the foil has been fully extended.

The foil is introduced into the apparatus in question by inserting the foil holder into a mounting block with the foil fully retracted in the holder and the end plate in place. The holder is positioned in such a manner that the end plate is seated in a groove in the gate which covers the sample port of the mounting block. The gasketed coupling nut is put on and tightened to obtain a vacuumtight seal between the foil holder and the mounting block. The gate-actuating lever of the mounting block is then placed in the "open" position, which movement uncovers the sample port and at the same time slides the end plate a sufficient amount to expose the inner chamber. The handle of the holder is then rotated, which movement extends the foil. Additional rotation of the handle when the foil is fully extended results in rotation of the foil so that, for example, either side may be counted in a Logac-L.

Rotation of the knob under the cap on the handle of the holder opens or closes the forceps which grip the foil. When the cap is in place, the knob is disengaged from the forceps by a clutch arrangement. The forceps are then free to slide in or out of the holder.

4.7 *Auxiliary Calorimetry Equipment.* (a) *Thyratron Heater Control.* The stability of the calorimeter bath temperature (Chap. 10) is an important factor in assuring precision in the measurement of the energy released in radioactive decay. One of the methods used for controlling the bath temperature uses a thyratron heater control. The original thyratron heater control was designed by J. W. Heyd at the Dayton Project, and this control was modified by C. E. Hites and H. L. Cook, Jr., at Mound Laboratory. The control of the calorimeter bath temperature to within ±0.002°C is possible with this equipment.

The correct operation of this circuit depends upon the proper application of two bias voltages to the grid of the thyratron V-2 (Fig. 9.41). A negative d-c voltage, which is obtained from the half-wave rectification of the alternating voltage appearing at the secondary of the transformer T-1, is provided at the lower contact on connector CN-1. A negative half-wave voltage which is obtained from the phase-shift network consisting of R-5, P-1, R-6, and C-2 is continuously diode-coupled to the thyratron grid. The diode coupling stage (V-1, Fig. 9.41) functions as a clipper circuit that prevents the application of positive half-wave voltage excursions to the thyratron grid, thereby preventing excessive thyratron-grid-current flow.

A mercury thermoregulator, which is immersed in the calorimeter bath, is connected across connector CN-1. The expansion of the mercury in the thermoregulator, which results from an increase in the

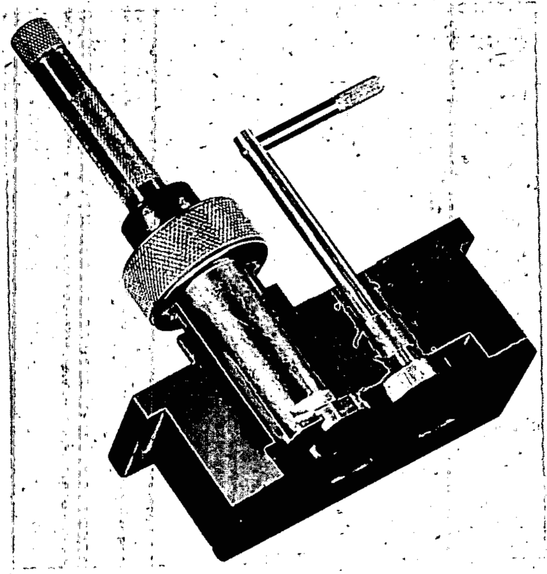


Fig. 9.39—Foil holder in mounting block, end plate being moved.

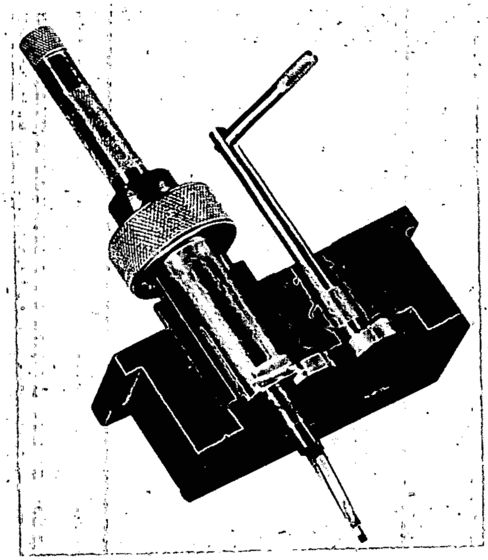


Fig. 9.40—Foil holder in mounting block, foil fully extended.

calorimeter bath temperature, will complete the circuit across connector CN-1; hence the negative d-c potential will be applied to the grid of the thyratron.

The application of both negative potentials to the thyratron grid will cut off this tube, and no thyratron anode current will flow through the bath heater unit; whereas the application of the negative half-wave voltage, by itself, to the thyratron grid will permit the tube to conduct and thereby supply anode current to the bath heater unit.

The setting of control P-1 regulates the amount of current supplied to the bath heater unit.

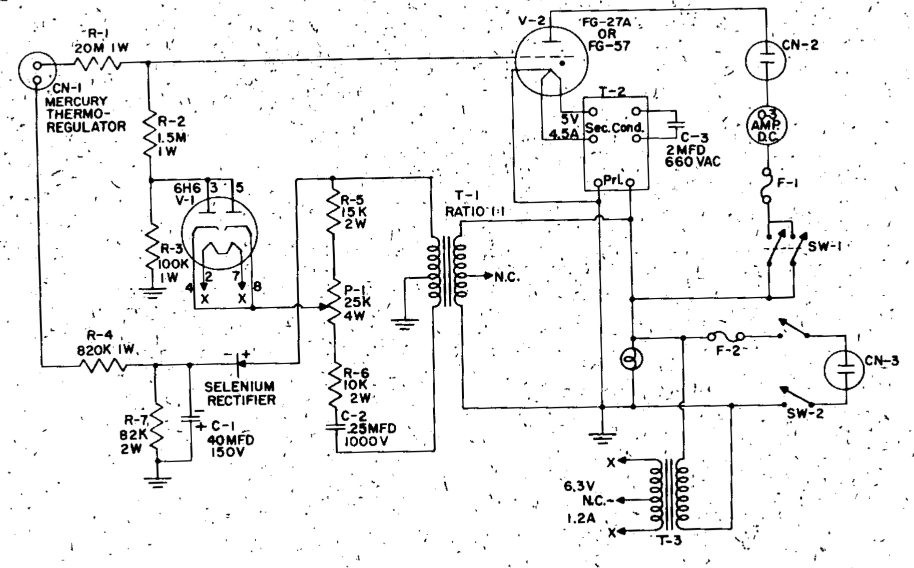


Fig. 9.41—Calorimeter thyratron heater control.

(b) *Proportional Bath Control.* The control of calorimeter bath temperatures to within 0.001°C presents a variety of problems. The development of a proportional-type controller (based on a Leeds & Northrup Company circuit)[46] for bath-temperature regulation has resolved most of these difficulties. In this apparatus the signal to the controller, which signal is caused by a change in bath temperature, is taken from a resistance bridge thermometer and fed to a galvanometer in the controller, which galvanometer reflects a wide beam of light onto a photoelectric cell. Deflection of the galvanometer changes the light flux on the photocell which changes the current delivered by a thyratron to the bath heater. For a steady deflection of the galvanometer a constant bridge-thermometer voltage is implied; this means a constant power into the bath which, when added to the power of stirring and other constant sources of power, just balances the power leak from the bath to the environment. Figure 9.42 shows the bridge thermometer with two opposite arms of the bridge contained in each of the thin-walled brass tubes. A top view of the proportional controller, showing the galvanometer and photocell, is shown in Fig. 9.43.

(c) *Platinum-Manganin Bridge Thermometer.* To facilitate observations of the bath temperature at the calorimeter control console (Fig. 10.5), a platinum-manganin bridge thermometer was developed. The principle of operation utilizes the temperature coefficient of resistance of the bridge winding. For a fixed current through the bridge the voltage change in the bridge is calculated from

$$E = IR\rho t$$

where I = half of the bridge current in amperes
R = resistance of one arm of the bridge
ρ = temperature coefficient of resistance of platinum
t = temperature change of the bath

The bridge is connected into a typical Wheatstone-bridge arrangement, as shown in Figs. 9.44 and 9.45, to realize the fullest sensitivity. Figure 9.46 shows the construction of the thermometer where the coil-form dimensions are chosen so as to minimize air spaces and, hence, reduce the time of response of the thermometer.

This circuit has a sensitivity of about 2.5 μv per 0.001°C and a time constant (speed) of 0.067 $\sec^{-1}$. The time to reach within 0.01 per cent of equilibrium is 2.3 min (see reference 47).

4.8 *Radio-frequency Electrodeless Discharge Exciter Unit (by John S. Stanton).* A radio-frequency electrodeless discharge exciter unit was designed for the purpose of ionizing polonium, or other material, inside a specially designed quartz discharge tube for atomic and molecular spectra studies.[48]

The major requirements were that the equipment supply a maximum radio-frequency power of 500 to 750 watts (or sufficient power to produce a discharge-tube temperature of 500°F) over a frequency range of from 10 to 30 Mc/sec. In addition, frequency and power output were to be adjustable and reproducible over the specified ranges.

A surplus Signal Corps radio transmitter BC-610E (part of radio set SCR 399) was found to meet these requirements after some modifications and additions.[49] A photograph of the modified BC-610E is shown in Fig. 9.47.

Experiments with a sample discharge tube showed that the tube could be fired and the tube temperature requirements met by using metal sleeve electrodes slipped over the ends of the tube. The tube is fired and the arc maintained by connecting the electrodes across the appropriate number of turns of the output tank coil. Since the tube was to be used on a special narrow optical bench, a remote tank circuit was necessary. Radio-frequency power is fed from the main unit to the coupling unit by means of a tubular 300-ohm unshielded twin line. A circuit diagram of the coupling unit is shown in Fig. 9.48. The radio-frequency

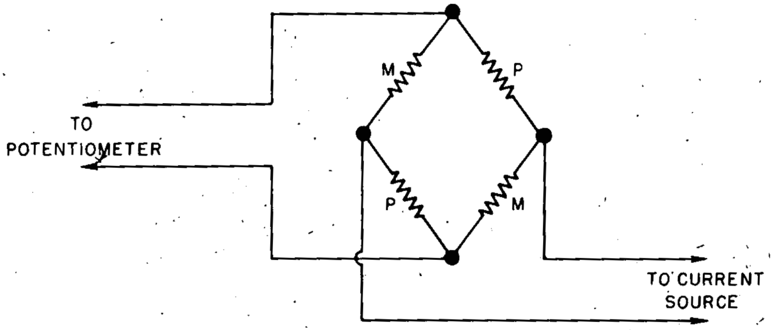


Fig. 9.44—Manganin-platinum bridge-thermometer schematic. P = 100 ohms, platinum wire; M = 100 ohms, manganin wire.

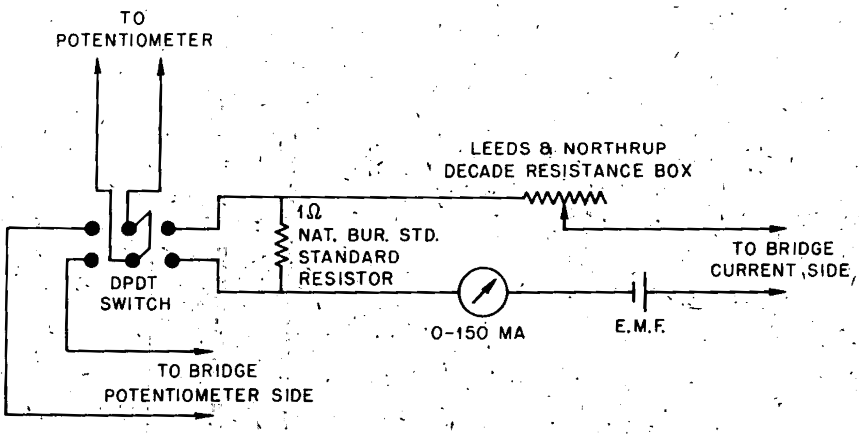


Fig. 9.45—Measuring circuit for manganin-platinum bridge thermometer.

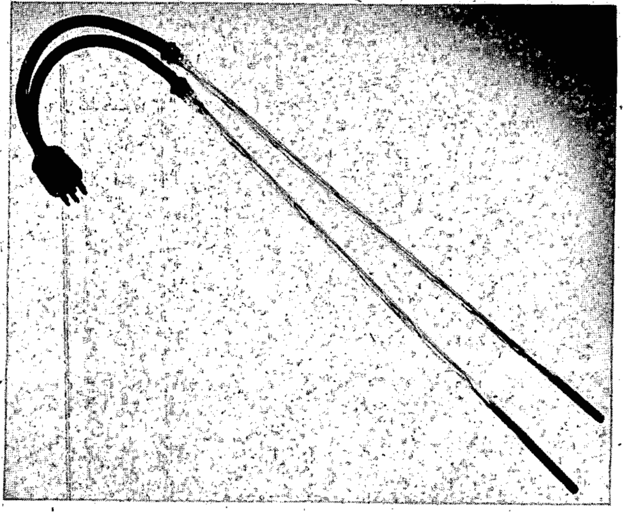


Fig. 9.46—Manganin-platinum bridge thermometer.

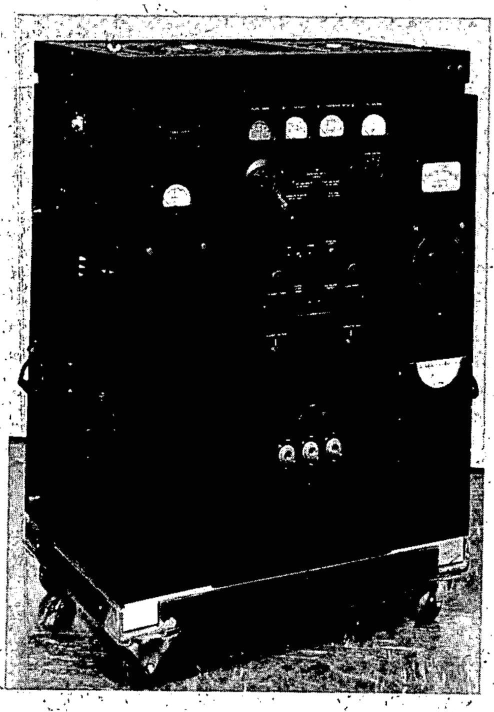
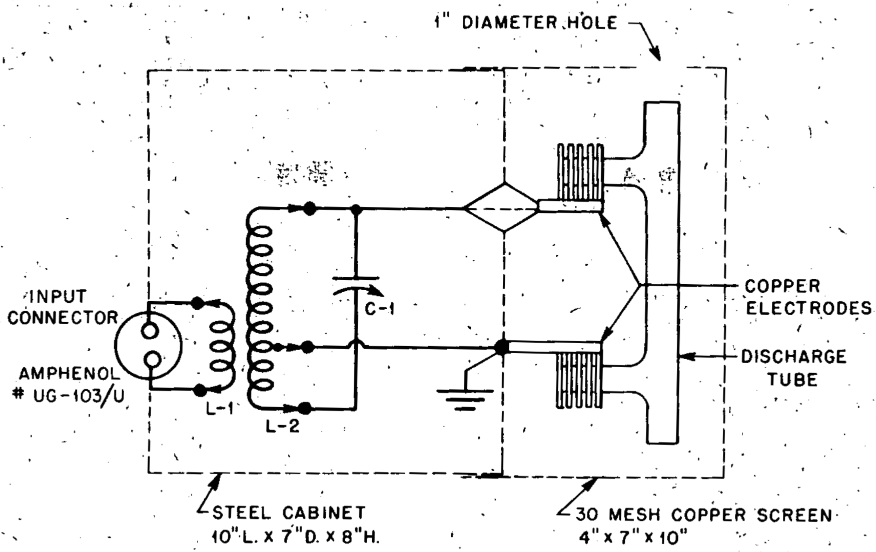


Fig. 9.47—Radio-frequency electrodeless discharge exciter unit.



C-1. 100-$\mu\mu f$ 6000-volt air condenser.

L-1. 10 to 17 Mc, two turns No. 10 AWG, $2^{11}/_{16}$-in.-diameter turns spaced $^{3}/_{32}$ in.; 17 to 31 Mc, one turn No. 10 AWG, $1^{15}/_{16}$ in. in diameter.

L-2. 10 to 17 Mc, eight turns No. 10 AWG, $2^{1}/_{4}$-in.-diameter turns spaced $^{5}/_{16}$ in., coil tapped 1.75 turns from rotor end; 17 to 31 Mc, six turns No. 10 AWG, $1^{19}/_{32}$-in.-diameter turns spaced $^{13}/_{32}$ in., coil tapped 1.25 turns from rotor end.

(Note: All coils are silver-plated, and links are centered near the tap.)

Fig. 9.48—Coupling unit for radio-frequency exciter.

ground on the tank coil does not appear at the rotor end of the coil as would be expected but at a point approximately 20 per cent up from the rotor end. The remaining tank turns are the close optimum compromise for firing and maintaining the arc. Also indicated in Fig. 9.48 is a copper screen covering the discharge tube. This serves to reduce interference to radio communication services.

Two other discharge exciter units for higher frequency and lower power were supplied. These were a power oscillator adjustable over the frequency range of 50 to 300 Mc/sec and a converted surplus radar transmitter AN/APT-5 operating over the frequency range of approximately 300 to 1500 Mc/sec. Both units supplied about 50 watts of power.

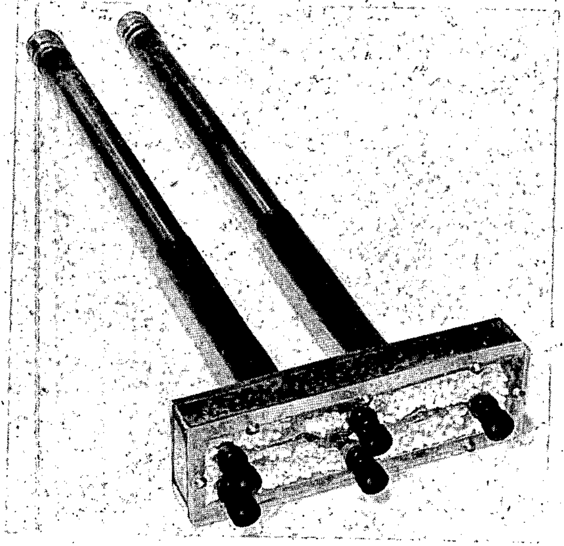


Fig. 9.42 — Bridge thermometer.

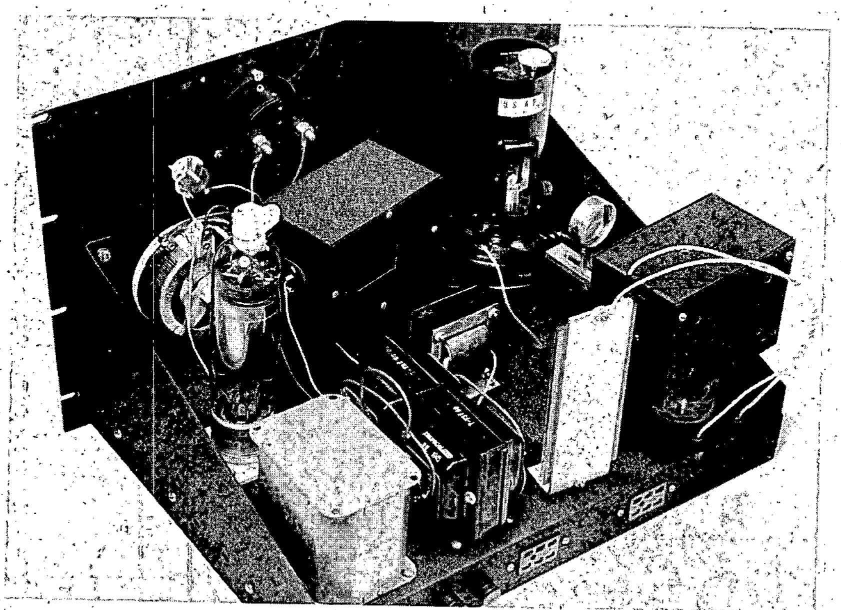


Fig. 9.43 — Proportional controller, top view.

REFERENCES

1. J. J. Sopka and K. S. Page, Report on Alpha Monitors, Final Report No. 8, Report MLM-M-1335, July 13, 1944, pp. 1-3.
2. J. J. Sopka and K. S. Page, Report on Alpha Monitors, Final Report No. 8, Report MLM-M-1335, July 13, 1944, pp. 5-7.
3. J. J. Sopka and K. S. Page, Report on Alpha Monitors, Final Report No. 8, Report MLM-M-1335, July 13, 1944, pp. 7-8.
4. J. J. Sopka and K. S. Page, Report on Alpha Monitors, Final Report No. 8, Report MLM-M-1335, July 13, 1944, pp. 8-10.
5. R. F. Wehrmann, Pencil-type Ionization Chambers, Ad Interim Report No. 6, Report MLM-M-31, Feb. 12, 1947.
6. S. De Benedetti, Low-geometry Instruments for the Measurement of Strong Alpha Samples, Final Report No. 22, Report MLM-M-419, Jan. 24, 1946.
7. S. De Benedetti, J. W. Heyd, C. Pittenger, L. Powers, C. Brenneman, and M. L. Curtis, Low-geometry Attachment for Methane-flow Proportional Alpha Counter, Final Report No. 47, Report MLM-M-270, Oct. 7, 1947.
8. L. B. Gnagey, Low-geometry Attachment for Methane-flow Proportional Alpha Counter (Supplementary Drawings for Final Report No. 47), Report MLM-287, Dec. 22, 1948.
9. J. A. Simpson, Jr., A Manual for the Proportional Alpha Counter, Report MDDC-46, May 8, 1945.
10. P. E. Ohmart, Investigation of a Method of Producing an Electric Current from Radioactivity, Report MLM-521, Dec. 1, 1950.
11. P. E. Ohmart, J. Appl. Phys., 22: 1504-1505 (1951); W. H. Waldo, J. Appl. Phys., 23: 290 (1952).
12. P. E. Ohmart, J. H. Hutchinson, E. H. Daggett, J. W. Heyd, and J. S. Stanton, The Radioelectric Effect, Report MLM-629, Nov. 1, 1951.
13. Lord Kelvin, Mathematical and Physical Papers VI, Cambridge, 1911.
14. F. J. Shon, private communication, May 3, 1951.
15. P. E. Ohmart and J. W. Heyd, Progress Report, Report MLM-M-69, Mar. 1–15, 1947.
16. T. I. Davenport and T. E. Eyles, Progress Report, Report MLM-368-3, April, May, and June 1949, pp. 643-651.
17. C. E. Hemler, Operating and Maintenance Manual for the Wall-mounting Gamma Monitor, Model CIT-8, Report MLM-566, June 1, 1951.
18. P. A. Tucker, Concentration Cells Operating Manual, Report MLM-536-1, Dec. 15, 1950.
19. P. L. Kirk, R. Craig, J. E. Gullberg, and R. Q. Boyer, Anal. Chem., 19: 427-429 (1947).
20. R. G. Olt, H. R. Du Four, M. I. Gray, S. R. Orr, and J. H. Wright, A Remote Controlled Quartz-fiber Microbalance: Design, Construction, and Characteristics, Report MLM-1022, Dec. 7, 1954.
21. R. G. Olt, H. R. Du Four, M. I. Gray, and J. H. Wright, A Remote Controlled Quartz-fiber Microbalance: Fabrication of Quartz Components, Report MLM-1023, Dec. 7, 1954.
22. G. L. Fox, P. J. Lowry, and E. A. Rembold, Some Effects Due to Weighing Polonium on a Quartz-fiber Microbalance, Report MLM-345, Apr. 14, 1949.

23. C. V. Boys, Phil. Mag., 23: 489 (1887).
24. R. Threlfall, Phil. Mag., 30: 99 (1890).
25. A. H. S. Holbourn, J. Sci. Instr., 16: 331 (1939).
26. J. S. Tapp, Can. J. Research, 6: 584 (1932).
27. H. V. Neher, "Procedures in Experimental Physics," John Strong, ed., pp. 205-206, Prentice-Hall, Inc., New York, 1938.
28. P. L. Kirk and F. L. Schaffer, Rev. Sci. Instr., 19: 785 (1948).
29. T. J. O'Donnell, D. Di Costanzo, T. Garner, J. Getzholtz, V. Hawley, W. Mankawich, and F. Pearson, Drawing and Working Quartz Fibers, Argonne National Laboratory, Report A-3953, March 1946, pp. 1-7.
30. T. J. O'Donnell and W. Mankawich, private communication, May 1947.
31. R. G. Olt, Improvements in Method and Equipment for Drawing Quartz Fibers, Report MLM-656, Jan. 29, 1952.
32. M. I. Gray and R. G. Olt, Special Applications of Quartz Fibers: The Fabrication and Use of Microtubing and Helices, Report MLM-1024, Dec. 7, 1954.
33. R. G. Olt and H. Du Four, Notes on Quartz-fiber Drawing, Information Report No. 35, Report MLM-M-199, July 30, 1947, p. 1.
34. F. Joliot, J. chim. phys., 27: 119 (1930).
35. W. H. Power, A Modified Joliot Apparatus for the Study of Electrodeposition of Polonium, Report MLM-909, Oct. 28, 1953.
36. P. E. Ohmart, Six-unit Microassay Plating Control, Report MLM-46-7-47, July 15, 1946.
37. J. W. Heyd and P. E. Ohmart, Progress Report, Report MLM-214, Oct. 1–30, 1948, pp. 4, 6-19.
38. J. W. Heyd, P. E. Ohmart, and C. E. Hites, Four-unit Plating Controls, PC-4 and PC-5, Report MLM-467 (Revised), Aug. 1, 1949, p. 1.
39. W. C. Elmore and M. L. Sands, "Electronics: Experimental Techniques," National Nuclear Energy Series, Division V, Volume 1, pp. 401-405, McGraw-Hill Book Company, Inc., New York, 1949.
40. C. E. Hites, Progress Report, Report MLM-368-2, April, May, and June 1949, pp. 435-451.
41. W. H. Bradley, private communication, May 1950.
42. A. Abate, Proc. IRE, 33: 478-482 (1945).
43. R. L. Shipp, Jr., Progress Report, Report MLM-405-5, October, November, and December 1949, pp. 81-101.
44. R. L. Shipp, Jr., Rev. Sci. Instr., 23: 91-92 (1952).
45. G. H. Brown, C. N. Hoyler, and R. A. Bierwirth, "Radio-frequency Heating," p. 32, D. Van Nostrand Co., Inc., New York, 1947.
46. J. R. Parks, T. J. Beasley, K. C. Jordan, and F. J. Shon, Progress Report, Report MLM-502, July 10 to Oct. 2, 1950, pp. 111-141.
47. J. R. Parks, Progress Report, Report MLM-319, Apr. 1–30, 1949.
48. D. J. Hunt and D. L. Timma, Progress Report, Report MLM-535, Oct. 30, 1950, to Jan. 22, 1951, p. 8.
49. J. S. Stanton, Progress Report, Report MLM-379-2, July, August, and September 1949, p. 341.

Chapter 10

CALORIMETRY

By Adrian J. Rogers

1. INTRODUCTION

A calorimeter is an apparatus for measuring quantities of heat; the first law of thermodynamics, namely, the principle of the conservation of energy, forms the basis of measurement by calorimetric methods. It is the aim of all calorimetric methods to dissipate the incoming energy in a medium, using the effect on the medium as a measure of the incoming energy. Calorimeters are especially useful for the quantity assay of alpha-particle-emitting radioactive isotopes; for example, those isotopes which have been incorporated into neutron sources and alpha sources.

Calorimeters have been used to measure the rate of heat or the total amount of heat generated from various sources. In 1903 Pierre Curie and A. Laborde[1] first used a calorimeter to measure the heat generated by the energetic particles from radioactive disintegrations. They used two matched Dewar flasks, one containing 1 g of a mixture of about one-sixth by weight of radium bromide in barium bromide, and the second flask contained 1 g of barium bromide. Based on the observed steady-state temperature difference between flasks, they were able to estimate the energy released by the radium bromide. Later experimenters[2] confirmed their results and improved upon their calorimeter.

In 1913 Rutherford and Robinson[3] used small platinum coils, attached to the inside of duplicate tubes, which served as two arms of a Wheatstone bridge (the other two arms consisted of manganin coils) in a calorimetric method of determining the heat produced by 1 g of radium in equilibrium with its short-half-life products. In this case the calorimeter either could be used as a null instrument or could be calibrated against known heating rates produced by an electric heater. This method for the determination of the quantity of heat generated is called "twin-differential" calorimetry and remains the most satisfactory system in many applications. The twin calorimeter is one among the many types of isothermal calorimeters and has one major advantage, that of compensating for the changes in the environment because of the presence of the second calorimeter. The first calorimeter contains the power source. It is this calorimetric method which provided the basic design principles for the Mound Laboratory calorimeter.

2. HISTORICAL BACKGROUND

The use of calorimeters at the Dayton Project and at Mound Laboratory dates from late 1944. Prior to this time polonium was assayed by electronic counters; however, the higher precision attainable with calorimeters as compared to the alpha-counting equipment available at that time recommended the use of calorimeters for the routine assay of neutron sources and alpha sources. In 1945, the workers at the Dayton Project envisaged the following benefits from use of calorimeters:

1. Polonium quantity-assays could be made with much greater accuracy than the existing assay by alpha counters.
2. The very low geometry alpha counters (Logac-L) used in the purity assay of samples could be standardized by calorimeters.
3. The calorimeters could aid the research program involving the physics and chemistry of polonium.
4. The half life of polonium could be redetermined calorimetrically with much greater precision than had previously been possible.[4–6]

The formation of two calorimetry groups, a Research Group and an Assay Group, were based upon these considerations. The Research Group developed faster, more sensitive, and more accurate calorimeters and essential auxiliary equipment. The Assay Group performed routine assays with the calorimeters that were designed and constructed by the Research Group.

The Research Group considered all types of calorimeters and decided that a differential resistance-bridge calorimeter, based on the Rutherford-Robinson calorimeter,[7–10] would be most suitable for their purposes. By the end of 1945, two such calorimeters were constructed by the Research Group and put into operation by the Assay Group. These calorimeters had a speed of about 2 hr and a precision of about 1 per cent with an accuracy of 2 per cent. It has been found that the factors which limit the precision of calorimetric measurements are to be found within the calorimeter, the environment of the calorimeter, and in the response of the calorimeter to its environment.

Much of the year 1946 was spent in improving the basic calorimeter design. An instrument with 0.15 per cent precision was constructed, but it had a speed of 2 days for a single sample assay. This particular instrument was considered to be too slow and fragile for routine assay purposes, but it was useful as a temporary standard in calorimetry and was suitable for very accurately measuring the half life of polonium. A microcalorimeter was constructed in 1946 which measured 200 mc of polonium with a precision of about 2 per cent.

Advances in calorimeter construction techniques and new materials of construction have been continuously incorporated into the Mound Laboratory calorimeters until at this time the present calorimeters are twice as fast, ten times more precise, about twenty times as accurate, ten to seventy times as sensitive, much more versatile, and much more rugged than those calorimeters developed by 1946.

3. THEORY OF CALORIMETRY

3.1 *Definitions.* (a) *Speed (Time of Response).* The speed of a calorimeter (a function of the construction) is the time elapsed between the insertion of a sample into the calorimeter and the arrival of the calorimeter and the sample to within 0.01 per cent of the equilibrium temperature. Since the Mound Laboratory calorimeters follow Newton's law of cooling very well, the time constant λ in the mathematical expression of this law,

$$T = T_{\max} e^{-\lambda t}$$

where T is the temperature in degrees centigrade and t is the time in seconds, is a function of the calorimeter speed. A precise determination of λ requires the solution of a second-order partial differential equation, based on the radial flow of heat in concentric cylinders having different thermal conductivities and unit heat capacities. Solutions to the type of heat-flow equations involved are adequately described in the literature.[11–14]

(b) *Precision.* The precision of a calorimeter is the ability to reproduce readings for a given sample.

(c) *Accuracy.* The accuracy of a calorimeter is the degree to which the absolute sample magnitude is determined.

(d) *Sensitivity.* The sensitivity of a calorimeter, which is conveniently expressed in units of microvolts per millicurie, is calculated from a knowledge of the thermal conductivity of the materials of construction of the calorimeter, the temperature difference across the cylindrical shell of the gradient medium, the inner and outer radii of this shell, the temperature coefficient of resistance of the bridge winding, and the bridge current. The observed Wheatstone-bridge potential in microvolts, recorded for a sample, is converted into millicuries of activity by multiplying this potential by the reciprocal of this derived factor.[15]

(e) *Thermel.* A thermel is a temperature detector and may be a resistance whose magnitude changes with temperature, a thermoelectric couple, a thermometer, a bolometer, or any other temperature-sensitive device.

(f) *Heat-distribution Error.* The heat-distribution error of a calorimeter is defined as the maximum per cent difference between the measured values of a small constant electric power source placed at various positions in the available sample volume. This error represents the maximum error that could be expected from failure of the heater to reproduce the heat flow of the sample. An alpha-emitting compound with an accurately known half life can serve to replace the electric power source.

(g) *Noise.* As used here, noise is any output of the calorimeter circuit that tends to obscure the information coming from the calorimeter. The precision of the measurement of the signal (information) is high when the signal-to-noise ratio is high. Conversely, for low signal-to-noise ratios, the precision of the measurement of the signal is low. Where the signal-to-noise ratio is less than 1, it is possible to use autocorrelation principles[16,17] to derive a measure of the signal. As an example of a noise source, consider the fluctuations of bath temperature induced by the stirrer. These are point-to-point fluctuations and are not average bath-temperature fluctuations. Hence, only fractional cancellation is effected by twin-differential calorimeters, and these bath-temperature fluctuations appear in the signal output of the calorimeter as noise.

3.2 *Operation of a Calorimeter.* Several methods of operating a steady-state resistance-bridge-type calorimeter are available. In the replacement method a sample is run, removed from the calorimeter, and replaced by a calibrating heater which is used to duplicate the bridge potential produced by the sample. The sample value is determined from the heater current measurement. This method guards against sudden changes in calorimeter sensitivity, but it has the disadvantage of having to reach temperature equilibrium in the calorimeter on two separate occasions.

The calibration method of calorimetric measurement utilizes previously obtained curves for sample evaluation. In this system the measurements of the equilibrium bridge potential are made for a series of heater currents, and the results are plotted as curie equivalents. Sample values are determined by referring to the graph and selecting the sample curie value corresponding to the observed bridge potential. Occasional heater runs are required to check the calorimeter calibration curve.

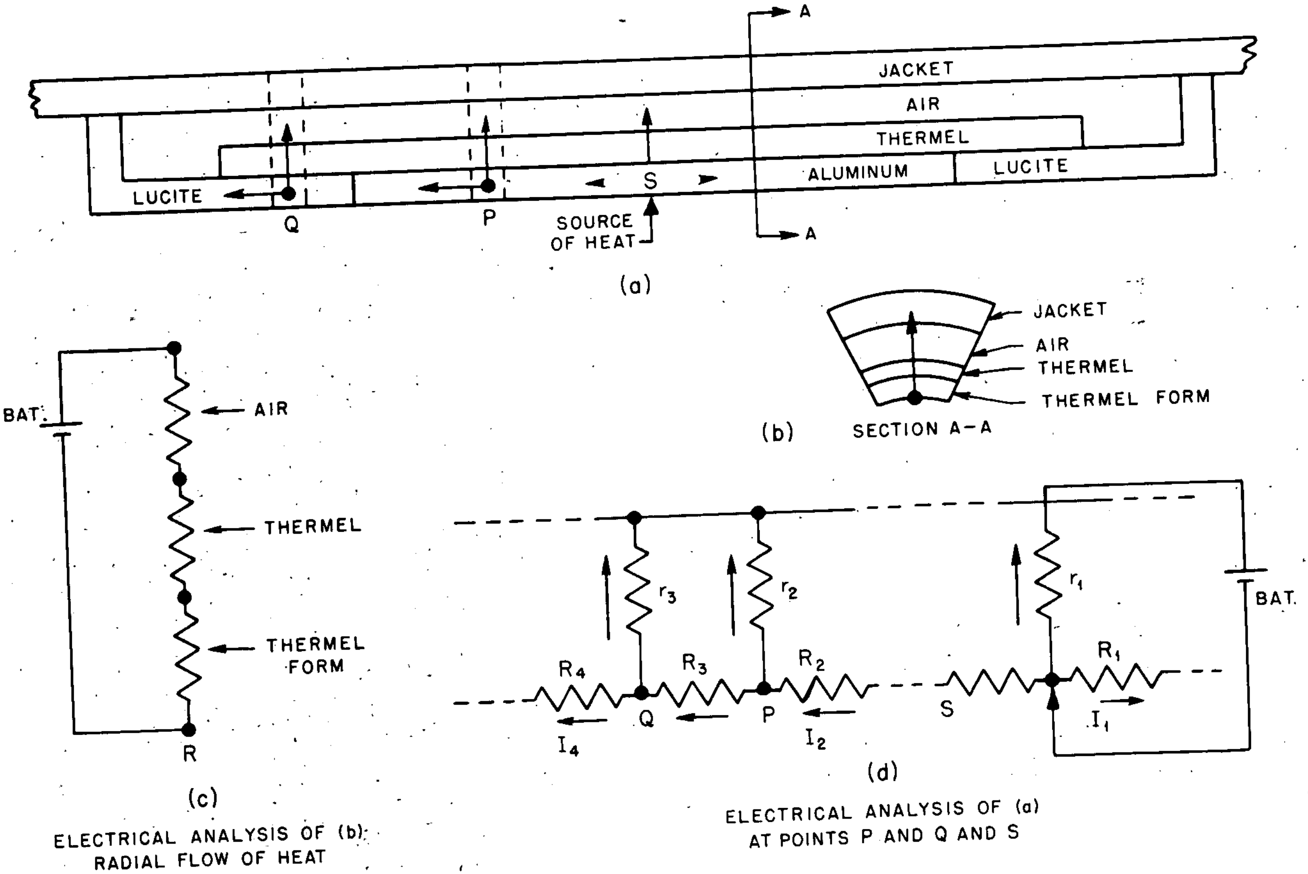
Satisfactory measurements of a sample can be made by simultaneously running the sample in one half of a calorimeter and running a heater in the other half. This has been named the "differential method" of calorimetric assay. It can be shown that it is not necessary for equal powers to be dissipated in both halves of the calorimeter for this method to be valid. An investigation of the theory involved in an evaluation of this method of assay will show that only constant factors are involved and that the heater side in the differential calorimeter is used only as a proportional reference point.[18] A description of this method of calorimetric assay is given in Sec. 3.4.

3.3 *Electrical Analogues.* Thermal problems in the unsteady (or transient) state are often solved by electrical analogues. This use of electrical analogues results from the mathematical difficulties inherent in the solution of the partial differential equations which represent heat flow. The steady-state problem of heat-distribution error also involves the solution of a partial differential equation. A d-c electrical analogue can be set up mathematically, and this close approximation, although tedious, can be solved by algebraic methods.

Thermal conductivities can be replaced by electrical resistivities, temperatures by voltages, heat flow by electrical current, and heat capacities by electrical capacitances. In the steady state, heat capacities do not affect the flow of heat; hence, in the electrical analogue, capacitances can be neglected.

One problem in calorimetry was the investigation, by electrical analogues, of the characteristics and relative merits of various thermel constructions and types of calorimeters. The problem is to build a network of resistance which would distribute an impressed current similar to the distribution of heat in passing from a sample in a calorimeter out through the thermel and air gap. The network evolved must be quite flexible in order to satisfy all types of calorimeters, and it must be conveniently laid out so that voltages and currents in the network can be determined accurately by using a potentiometer.

A small longitudinal element of a calorimeter thermel would look as shown in Fig. 10.1a. Assuming that the heat source in a calorimeter is at point S, heat will flow, when the steady state is reached, radially and longitudinally simultaneously at each point of the thermel, as at points P, Q, and S. At each point the heat flow will experience a resistance to flow which is a function of the dimensions of the element selected at that point and the inverse of the thermal conductivity of the material through which the heat must flow from that point. If, in the electrical



(c)

ELECTRICAL ANALYSIS OF (b): RADIAL FLOW OF HEAT

(d)

ELECTRICAL ANALYSIS OF (a) AT POINTS P AND Q AND S

Fig. 10.1—D-c electrical-mechanical calorimeter equivalents.

analogy, a resistance can be selected that is proportional to the inverse of the thermal conductivity (which can be called "thermal resistance"), the problem can be handled. Figure 10.1d shows the electrical equivalent of the calorimeter, with r_1, r_2, r_3, etc., representing the radial resistances to current flow and R_1, R_2, and R_3, etc., representing the longitudinal resistances to flow. For a given current flow the voltage readings taken at points like P, Q, and S will simulate a temperature distribution along the thermel in the analogous heat-flow case. The resistance network assumes the form shown in Fig. 10.2. Since the composition of the thermel form is to be studied, variable resistances were used for the longitudinal resistances R_1, R_2, R_3, etc. In this way the temperature distribution for various thermel constructions could be studied for a given heat input in a calorimeter.

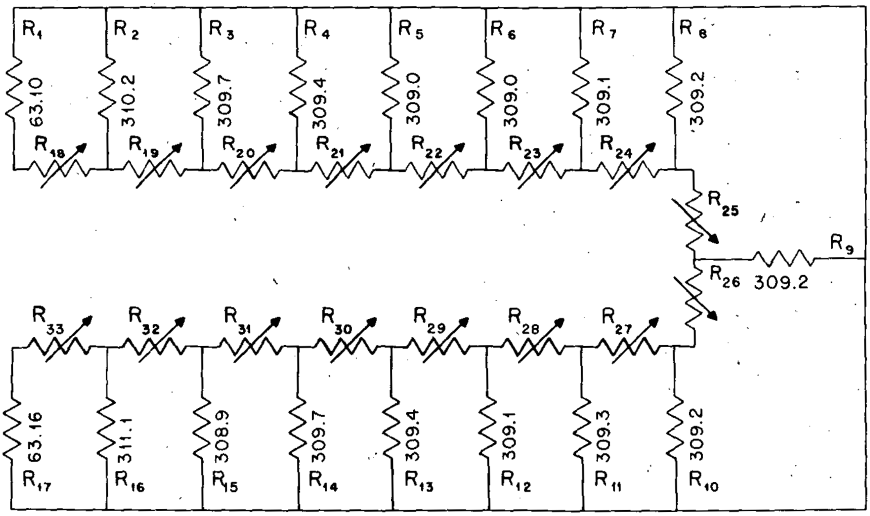


Fig. 10.2—D-c electrical analogue of a calorimeter.

Relative values of resistance are chosen according to the equation $R = kt/KA$, where t is the thickness of the section along the direction of heat flow, A is the area of the section perpendicular to the direction of heat flow, K is the heat conductivity of the section, and k is a constant factor to give the desired range of resistance in ohms. Following the above described principles, five different types of thermel construction have been simulated. The results of tests have provided the following useful information:[19]

1. The three-section thermel is the most satisfactory type. This thermel has a good conducting central section to give a flat temperature distribution and is followed on each end by a poor conducting section. The bridge winding extends over all three sections to a length dependent upon permissible loss of heat around the ends of the thermel.
2. In any kind of calorimeter design, guard-ring action (which is equivalent to high resistance to current flow) is beneficial. However, the advantages of guard-ring action are nearly offset by the complexity of this type of calorimeter. "Guard ring," as used here, refers to a heat baffle.
3. A guard-ring calorimeter will have from one-third to three-fourths the heat-distribution error of a straight twin calorimeter.

3.4 *Fundamental Calorimeter Equations.* The energy of the polonium alpha is known, and, since the number of disintegrations per second in a curie is fixed by definition, it is possible to determine the amount of energy which each curie will give off, per unit time, as kinetic energy of alpha particles. The penetration of the alpha particles is insufficient to permit them to leave the calorimeter; hence their kinetic energy is manifested as heat. From the law of conservation of momenta the recoil energy of the lead atoms produced in polonium decay can be calculated. The sum of these two heat quantities (alpha and recoil energy) will represent the total heat output of a curie of polonium. The energy given off by polonium as gamma radiation is so small and the stopping power of the calorimeter for gammas is so slight that any thermal effect due to gamma radiation may be neglected.[20]

Based on the above-mentioned energy considerations, the heat equivalent of polonium can be derived. The total energy dissipated per polonium alpha emission is calculable from the following equations:

$$E_\alpha = m_0C^2 \left[(1 - \beta^2)^{-1/2} - 1\right] \text{ ergs}$$

$$E_{Re} = \frac{E_\alpha(E_\alpha + 2m_0C^2)}{2M_0C^2} \text{ ergs}$$

$$E_{Total} = (E_\alpha + E_{Re}) \text{ ergs}$$

where E_α = energy of the polonium alpha particle
m_0 = rest mass of the polonium alpha particle
C = velocity of light
$\beta = v/C$
v = velocity of the polonium alpha particle
E_{Re} = energy of the lead recoil fragment
M_0 = rest mass of the lead recoil fragment

2.54

Converting E_{Total} to joules by multiplying by 10^{-7}, and, since 1 joule is equivalent to 1 watt-sec,

$$E_{Total} = (E_\alpha + E_{Re})\, 10^{-7} \text{ watt-sec}$$

By multiplying E_{Total} by the number of disintegrations per second per curie (3.7×10^{10}) and taking the inverse of this factor, the heat equivalent of polonium is obtained. From values tabulated for E_α and E_{Re} (see reference 21), the heat equivalent of polonium is calculated as being 31.23787 ± 0.00920 curies/watt.

The operation of the steady-state calorimeter depends upon the equation

$$Q = \frac{k(T_1 - T_2)}{d}$$

where Q is the quantity of heat transferred per unit time per unit area between two boundaries, 1 and 2, a distance d apart; T_1 and T_2 are the temperatures at the respective boundaries; and k is the coefficient of thermal conductivity. This equation holds only for steady-state heat transfer.

In practice, the boundaries chosen are the inside and outside of a medium within which the sample is placed and which is itself suspended in a constant-temperature bath, leaving T_1 and Q as variables. Inside the medium (in this case a cylindrical tube) and surrounding the sample is a winding comprising the two opposite arms of a Wheatstone-bridge circuit, the other two arms of which are wound in a tube of identical construction suspended in the same bath. These two tubes are referred to as the "sample side" and the "dummy side" of the calorimeter.

When the sample has been in place long enough so that the steady state pertains, then

$$\Delta T = k'Q$$

where ΔT is the amount by which the internal temperature of the side in question has risen above the base or zero temperature which it had before the sample was placed in the calorimeter or the heater was energized, Q is the amount of heat passing per unit time per unit (mean) area through the gradient medium from the sample or heater, and k' is the inverse of k/d.

Since the Wheatstone-bridge potential is a function of the comparative resistance of the opposite pairs of arms, and since the resistance of the bridge windings will increase with temperature,

$$\Delta BP = k''Q$$

where ΔBP is the amount of change in bridge potential contributed by the side under consideration, assuming the functions mentioned above are linear. Defining a quantity S (the sensitivity) as being equal to k″, the change in bridge potential for each side of the calorimeter can be represented by the following equations:

$$\Delta BP_s = S_s Q_s$$

$$\Delta BP_D = S_D Q_D$$

where the subscripts s and D refer to the sample side and dummy side of the calorimeter, respectively. Assuming that both sides of the calorimeter contribute independently to the total change in bridge potential, and defining the contribution of the sample side as being the more positive value, then

$$\Delta BP_{Net} = \Delta BP_s - \Delta BP_D = S_s Q_s - S_D Q_D$$

Expressing the sensitivities in terms of microvolts per curie of polonium instead of in terms of microvolts per heat unit per unit time per unit area (the mean area is constant but undetermined),

$$\Delta BP_{Net} = S_s C_s - S_D C_D \tag{10.1}$$

where ΔBP_{Net} is the actual change in potential from zero (i.e., no sample, no heater) measured across the potential terminals of the bridge and C represents the curie value of the sample or the curie equivalent of the dummy heater as the subscript indicates. Equation 10.1 might be called the "basic equation" of the calorimeter.

A quantity F (the heater factor) is defined as the resistance of the heater times the constant 31.2379 which expresses the resistance of the heater in terms of the curie equivalent per current unit squared (I^2) rather than in ohms. For any heater, $C = I^2F$, and by substituting in Eq. 10.1,

$$\Delta BP = I_s^2 F_s S_s - I_D^2 F_D S_D$$

for the calibration condition where heaters are being run in both sides. For heaters connected in series, $I_s = I_D$, and

$$\Delta BP = I^2(F_s S_s - F_D S_D) = mI^2 \tag{10.2}$$

where m is a constant and is, in fact, the slope of the curve obtained by dividing the bridge potential deflection by the square of the current used for a single run. For a run in which the dummy side is not energized

$$\Delta BP = F_S S_S I^2 \tag{10.3}$$

The sensitivity S_S can then be evaluated from one determination, assuming the heater factor F_S to be known. The heater factor F_S is developed later. For a sample run

$$\Delta BP = C_S S_S - I^2 F_D S_D$$

and solving for the sample value

$$C_S = \frac{\Delta BP + I^2 F_D S_D}{S_S}$$

From Eq. 10.2

$$F_D S_D = F_S S_S - m = A \tag{10.4}$$

and the sample curie value is

$$C_S = \frac{\Delta BP + AI^2}{S_S} \tag{10.5}$$

Thus by two runs, one with no heater in the dummy half of the calorimeter and one with heaters in both calorimeter halves, and with a determination of sample-side heater resistance, the two quantities A and S_S are determined. Running an unknown sample with current flowing in the heater unit of the dummy half of the calorimeter permits the evaluation of the sample size by measuring the ΔBP and applying Eq. 10.5.

In practice it has been found that a greater accuracy is obtained if the calorimeter is run nearly at balance, i.e., if the voltage effect of the dummy heater nearly equals that of the sample. This can be accomplished if the sample size is known approximately, as by a gamma count. Equation 10.5, with $\Delta BP = 0$, becomes

$$C_S = \frac{AI^2}{S_S}$$

In order to effect all the measurements required by the above theory, the calorimeter circuit should be adjustable so that:

1. The bridge current is reproducible, since the Wheatstone-bridge potential depends upon the current through the bridge.
2. Bridge potentials are measurable.
3. Heater currents are measurable and capable of being set to a predetermined value.
4. Heater potentials are measurable to determine heater resistance.
5. A switching system capable of energizing either heater independently or both heaters in series is provided.

In practice, all voltages are measured by a Wenner potentiometer, and all currents are measured by this same instrument by observing the potential drop across standard resistors through which the currents flow. Figure 10.3 presents a schematic diagram of the calorimeter control circuit for a single calorimeter.

The heater factor F_s can be determined from adjustment of the switches in the calorimeter control circuit as follows: on position 10 of the selector switch, a potential (HP) is measured which is $^1/_{11}$ of that across the voltage divider. Positions 6 and 8 will give the potentials HPL_1 and HPL_2 between the ends of the voltage divider and the corresponding ends of the heater. The heater potential will then be

$$\text{Heater potential} = 11HP - HPL_1 - HPL_2$$

Measuring the current I at switch position 4, the heater factor F_S can be determined:

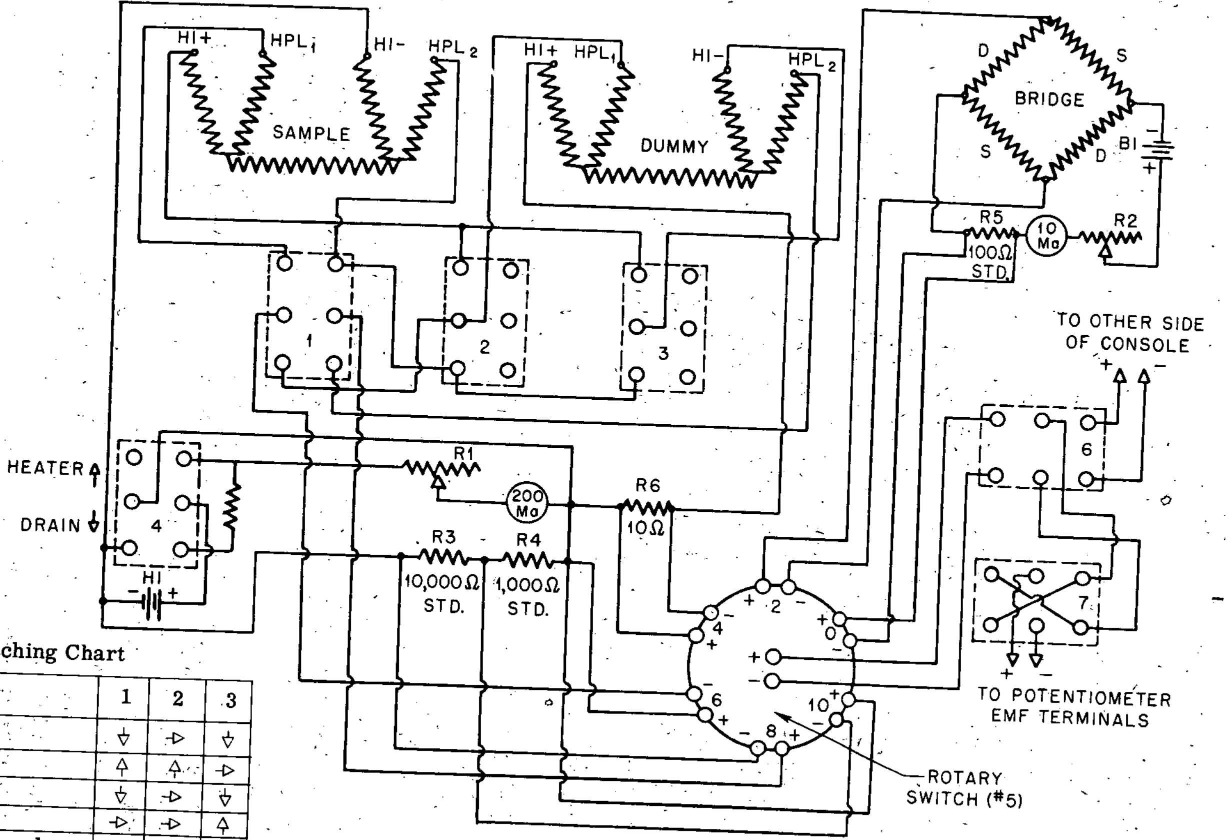
$$F_S = \frac{(11HP - HPL_1 - HPL_2) \times 31.2379}{I}$$

Also, by measuring the bridge potential at switch position 2 and subtracting the zero-point bridge potential, the sensitivity S_S is calculable from Eq. 10.3.

By setting switches 1, 2, and 3 as shown by the switching chart on the figure (Fig. 10.3) for a slope or "m" run, and reading bridge potential and heater current, the quantities m and A can be obtained from Eqs. 10.2 and 10.4 for a complete calibration.

Figure 10.4 shows a representative type of calorimeter in use at Mound Laboratory. Figure 10.5 shows a typical calorimeter console from which all data are read. Two calorimeters immersed in a constant-temperature bath are shown in Fig. 10.6.

3.5 *Calorimeter Error Limitations.* For a differential calorimeter run, the equation for calculating the curie value of a sample can be presented as



Switching Chart

Operation	1	2	3
Sample	▽	▷	▽
F_s and S_s	△	△	▷
F_D and S_D	▽	▷	▽
Calibration, m	▷	▷	△
Replacement sample	▷	▽	▷
Replacement heater	△	△	▷

Fig. 10.3—Control circuit for single calorimeter.

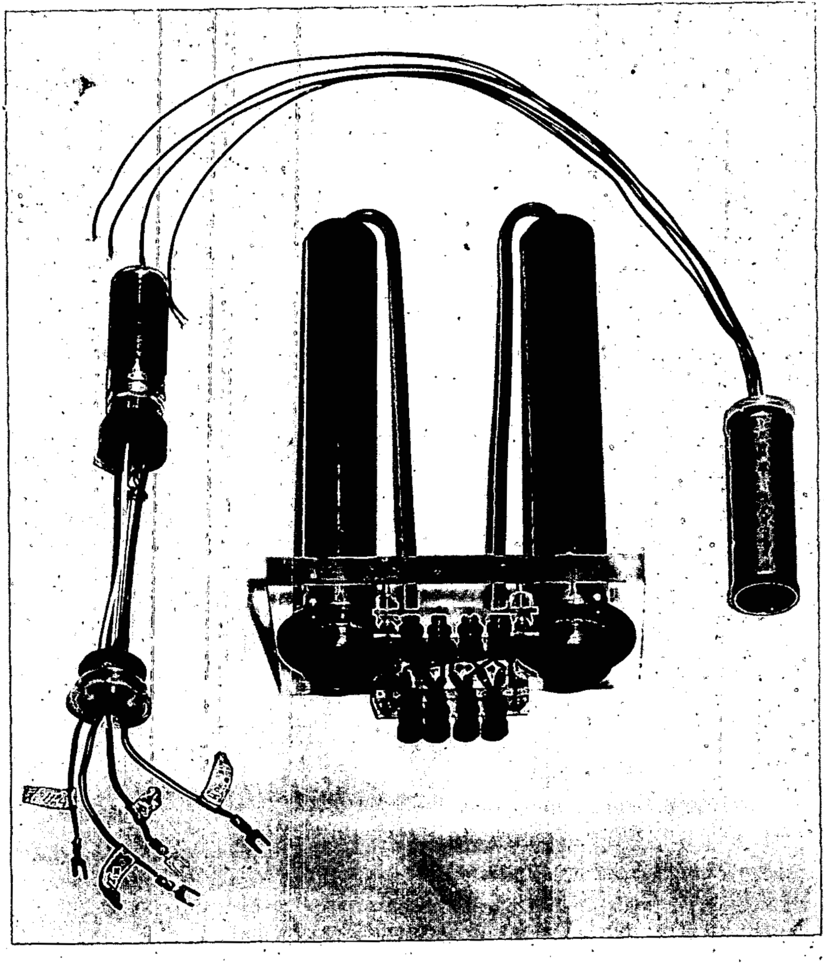


Fig. 10.4—Representative type of Mound Laboratory calorimeter.

$$C_S = 31.2379\ I^2R_S - \frac{(mI^2 10^4 + BP_0 - BP)\ 10^{-3}}{S} \qquad (10.6)$$

where C_S = sample value, curies
I = heater current, amperes
R_S = sample-side heater resistance, ohms
m = slope, microvolts per ampere squared
BP_0 = zero bridge potential, microvolts
BP = bridge potential during sample run, microvolts
S = sensitivity, microvolts per millicurie

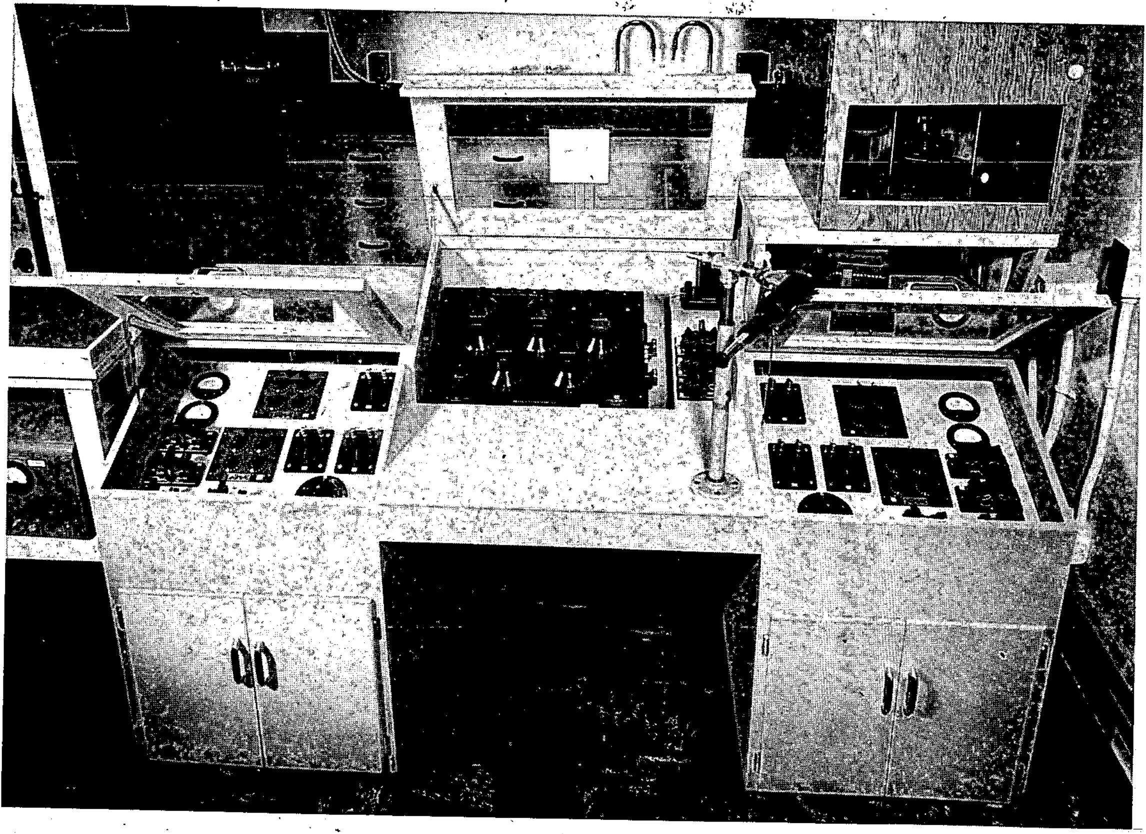


Fig. 10.5—Typical calorimeter console.

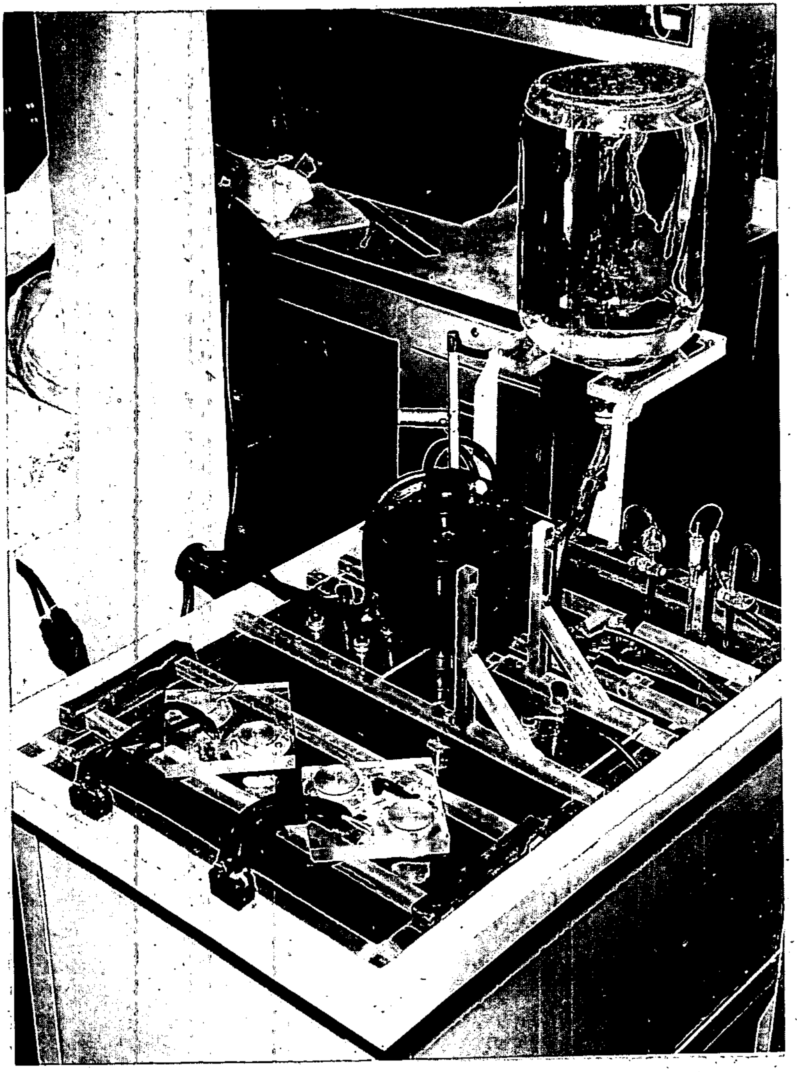


Fig. 10.6 — Two calorimeters immersed in a constant-temperature bath.

The precision of measurement of C_s is a function of the precision of measurement of each of the directly measured quantities. To determine what error is allowable in each of the directly measured quantities if a prescribed error in C_s is not to be exceeded, Eq. 10.6 is written

$$C_s = f(I, R_s, m, BP_0, BP, S) \tag{10.7}$$

Differentiation of Eq. 10.7 gives

$$\Delta C_S = \frac{\partial f}{\partial I} \Delta I + \frac{\partial f}{\partial R_S} \Delta R_S + \ldots \qquad (10.8)$$

In a set of repeated measurements it is assumed that each set of the ΔI's, ΔR_S's, etc., has a normal distribution. Therefore, if Eq. 10.8 is squared, the sum of all the cross terms, $\Delta I \cdot \Delta R_S$, etc., will vanish since there will be an even distribution of positive and negative terms. Thus, if there are n values of C_S,

$$\sum_1^n \Delta C_S^2 = \sum_1^n \left[\left(\frac{\partial f}{\partial I}\right)^2 \Delta I^2 + \left(\frac{\partial f}{\partial R_S}\right)^2 \Delta R_S^2 + \ldots\right] \qquad (10.9)$$

The original statement of the problem suggests the following treatment. In the absence of any knowledge to the contrary, and in view of the assumed normal distributions, it is postulated that

$$\left(\frac{\partial f}{\partial I}\right)^2 \Delta I^2 = \left(\frac{\partial f}{\partial R_S}\right)^2 \Delta R_S^2 = \left(\frac{\partial f}{\partial m}\right)^2 \Delta m^2 = \ldots \qquad (10.10)$$

If any of these products has a known value, this value should be inserted in Eq. 10.9 and moved to the left side of the equality sign.

If the assumption stated in Eq. 10.10 is introduced into Eq. 10.9,

$$\Delta C_S^2 = n\left(\frac{\partial f}{\partial q}\right)^2 \Delta q^2$$

Here n is the number of independent variables in Eq. 10.7 which have unknown values fitting Eq. 10.10, and q is a generalized symbol for the independent variables, now all assumed to have equal effect. For a prescribed value of ΔC_S, it is now possible to find the corresponding allowed value of Δq:

$$\Delta q = \frac{\Delta C_S}{\sqrt{n}\,(\partial f/\partial q)}$$

This equation can be used with Eq. 10.6 and, with reasonable assumptions as to numerical values of the independent variables as they occur in practice, to find the various allowed values of the Δq's. Reasonable values of permissible variation in the independent variables for the Mound Laboratory calorimeters are:[22]

$\Delta C_S = 0.001$ curie

$\Delta m = 0.195S$ μv/amp^2

$\Delta BP_0 = \Delta BP = 0.5S$ μv

$\Delta S = 0.005S$ mc/μv^2

$\Delta I = \Delta R_S = 0$

The sensitivity S of a calorimeter is defined as

$$S = \frac{\gamma_1 Ri \ln (r_2/r_1)}{4\pi LK}$$

where γ_1 = temperature coefficient of resistance of bridge winding
R = total resistance of bridge winding
i = bridge current, amperes
r_2 = outer radii of the calorimeter shell under investigation
r_1 = inner radii of the calorimeter shell under investigation
L = length of cylinder through which heat is escaping
K = thermal conductivity of calorimeter material

3.6 *Accuracy, Range, and Precision of Calorimeters.* The calorimeters used by the assay group at Mound Laboratory must fulfill certain minimum requirements in order that sample magnitudes be measurable to prescribed precisions with a specified accuracy. This is accomplished by using standardized components in the measuring circuits, accurate measuring instruments, and stable current and voltage sources, and through minimization of calorimeter errors. From consideration of these factors the Mound Laboratory calorimeters have been developed to the status that:

1. The accuracy is of the order of 0.1 per cent.
2. The precision is better than 0.1 per cent.

3.7 *Measurement of Alpha, Beta, and Gamma Radiation.* For millicurie or curie amounts of radioactivity, a calorimeter assay can be made with much greater certainty than a particle-counting assay because of the independence of the calorimeter to the physical characteristics of the sample. Calorimetry is especially applicable to alpha emitters because of the high energies and short ranges of alpha particles.

The usefulness of the calorimeters at Mound Laboratory can be extended to include beta emitters after ascertaining that the beta particles give up their energy within the calorimeter proper. Since the beta particles are charged and have a finite range, this condition would usually be satisfied by calorimeters designed for alpha emitters. It is possible to measure beta disintegration rates with a calorimeter if the average energy of the beta particle is known.

With gamma rays the required mass of absorber in a calorimeter is so great that it is generally accepted that a gamma-ray calorimeter must operate at the temperature of liquid helium ($T \sim 4°K$) in order to reduce the heat capacity and radiation losses to such a level that the speed and sensitivity of the calorimeter are of reasonable magnitudes.

274

4. CALORIMETRIC ASSAY OF POLONIUM

4.1 *Assay Calorimeters.* The present Mound Laboratory calorimeters have been developed for the assay of alpha-particle-emitting isotopes; specifically, those incorporated into neutron sources and alpha sources. Since these sources may cover relatively wide ranges of activity, the calorimeters used should be capable of accurately measuring quantities of activity from less than 0.1 curie up to several hundred curies. In the Mound Laboratory calorimeters a precision of 0.1 per cent is attained, and experiments have indicated that the absolute error is generally less than 0.1 per cent for samples which encompass an activity range of greater than 1000 to 1.

4.2 *Comparison with Particle Counters.* Limitations existing in electronic particle counters restrict their usefulness to sample magnitudes of less than 10 curies, or about 10^{13} counts/min. Special low-geometry attachments (Chap. 9) are required for samples of this magnitude. Other conventional particle counters are limited to about 2 mc of activity. For these counters, sample-mounting procedures, self-absorption of sample activity, geometry considerations, spatial distribution of sample activity, and backscattering effects are some of the factors affecting the observed results. In a properly designed calorimeter the observed results are unaffected by these factors; however, heat-distribution errors, convection and radiation losses, bath-temperature fluctuations, etc., do affect the results and must be taken into account. In addition, the calorimetric assay method requires an accurate knowledge of the disintegration energy, mode of decay, half life, type of radioactive emission, etc., of the material being assayed before precise results are attained.

Discrepancies between the results obtained using different low-geometry attachments[23] led to a reevaluation of particle-counting procedures. The present absolute alpha-counting methods are based on the results of this study, and these methods produce results that are as precise as those obtained from calorimetric assays. In fact, particle counters supplement calorimeters to the extent that they extend the range of sample activities that are measurable to very low values. One advantage of particle counters is that they can be used to measure many samples in a shorter time than is possible with calorimeters.

4.3 *Comparison with National Bureau of Standards Ice Calorimeter.* In an attempt to determine the precision and accuracy of the Mound Laboratory type calorimeter, five polonium samples were sent to the National Bureau of Standards for assay in their ice calorimeter. The sample values obtained by the National Bureau of Standards checked the values obtained at Mound Laboratory to better than 0.1 per cent. The precisions achieved with the Mound calorimeters were equivalent to, or considerably better than, the National Bureau of Standards results as obtained with their ice calorimeter. The individual sample values obtained at Mound checked to within 0.1 per cent or better, and the largest average deviation between the values obtained at Mound and at the National Bureau of Standards was −0.09 per cent, the smallest being +0.05 per cent. A further comparison between calorimeter types can be made on the basis of the relative operating time required. At the National Bureau of Standards a person can assay two samples a day with the ice calorimeter. At Mound Laboratory one person can assay 5 samples a day with a resistance-bridge calorimeter.

5. SPECIAL APPLICATIONS

5.1 *Half-life Measurements.* The physical and chemical properties of polonium were not known with great accuracy during the early years of the Dayton Project. The value recorded for the half life of polonium was not known to the desired degree of accuracy, and, in 1945, an attempt to evaluate this constant by calorimetric methods was initiated. By October 1945, initial values for the half life were determined; the average value was 139 days. A 12-curie sample of polonium was used in these early experiments. Other measurements of the half life were made from time to time, and, in all, six determinations have been made with four different steady-state resistance-bridge calorimeters and five different polonium samples (Chap. 2, Sec. 2.3). These six values of the half life have been weighted and combined to give a grand-mean value for the half life of 138.4005 ± 0.0051 days (see reference 24).

5.2 *Reactor Flux Determinations.* Irradiated bismuth slugs are shipped to Mound Laboratory along with a statement of the channel number in the reactor and the total amount of polonium contained in the irradiated slugs at the time of shipment. It was observed that the calorimetric assay of the extracted polonium deviated from the figures received with the irradiated slugs by as much as 20 per cent. These discrepancies made bookkeeping quite uncertain and caused uncertainties in determining the efficiency of the separation process. To resolve this discrepancy, the Research Group adapted a calorimeter to accommodate a single irradiated-bismuth slug and which would be able to assay two of these slugs per day with a probable error of 0.1 per cent.

The calorimetric assay of a batch of slugs showed that the curie-value of the polonium formed in the slugs is directly proportional to the product of the neutron flux and the neutron-capture cross section along the channel in the reactor. The results of this assay determined the neutron-flux distribution along the axis of the reactor channel with a precision of at least an order of magnitude greater than it was known at that time. The assay results provided the reactor engineers with a means of obtaining a new calibration factor to determine the polonium content of a slug at the time of removal from the reactor. Calorimetric-assay data may also be used to determine the existence of any irregularities in the reactor neutron flux in the vicinity of control rods, cooling vents, reflectors, etc., provided that channels are available in these areas.

6. CONSTRUCTION FEATURES

6.1 *Calorimeter Baths and Bath-temperature Controllers.* The calorimeter baths in use at Mound Laboratory are constant-temperature units containing approximately 54 gal of distilled water which has a thermal capacity of 2×10^5 calories/deg. Water lost by evaporation is automatically replenished from an inverted 5-gal jar suspended over the bath (Fig. 10.6).

Ice-water mixtures are known to remain at a constant temperature if the mixture is well stirred. Mound Laboratory has experimented with a bath of this type (Fig. 10.7) which held approximately 20 gal of ice and water and required about 12 lb of ice per day to maintain the bath temperature to a constancy of better than 0.01°C. Bath-temperature fluctuations are presently controlled by a proportional-type controller. This controller is discussed in Chap. 9, Sec. 4.7b.

6.2 *Bath Stirring.* Considerable effort has been expended to determine the best method of stirring a bath for temperature uniformity. Vertical stirrers, with adjustable-pitch propellers, develop more nearly uniform bath-temperature conditions and are used almost exclusively in the Mound Laboratory calorimeter baths. The efficiency of stirring is checked by introducing small quantities of ink at various points of the bath surface and measuring the time for the ink to be distributed evenly throughout the bath. The greatest time observed was 15 sec; hence this indicates that temperature gradients cannot exist in the bath for times longer than this.

6.3 *Calorimeter Assembly.* The assembly of a differential-bridge calorimeter is shown in Figs. 10.4 and 10.8. Many variations in the construction of a calorimeter are possible, although certain features, such as the use of a Wheatstone-bridge arrangement for detecting temperature changes, remain fixed. Guard rings, different types of insulator materials, coil forms, wire diameters, etc., are some of the variables of construction. The design and construction of calorimeters require the use of materials chosen according to their thermal conductivities, densities, specific heats, temperature coefficients of resistance, etc. This information, together with a knowledge of the fundamental heat-flow characteristics, permits optimum calorimeters to be designed.

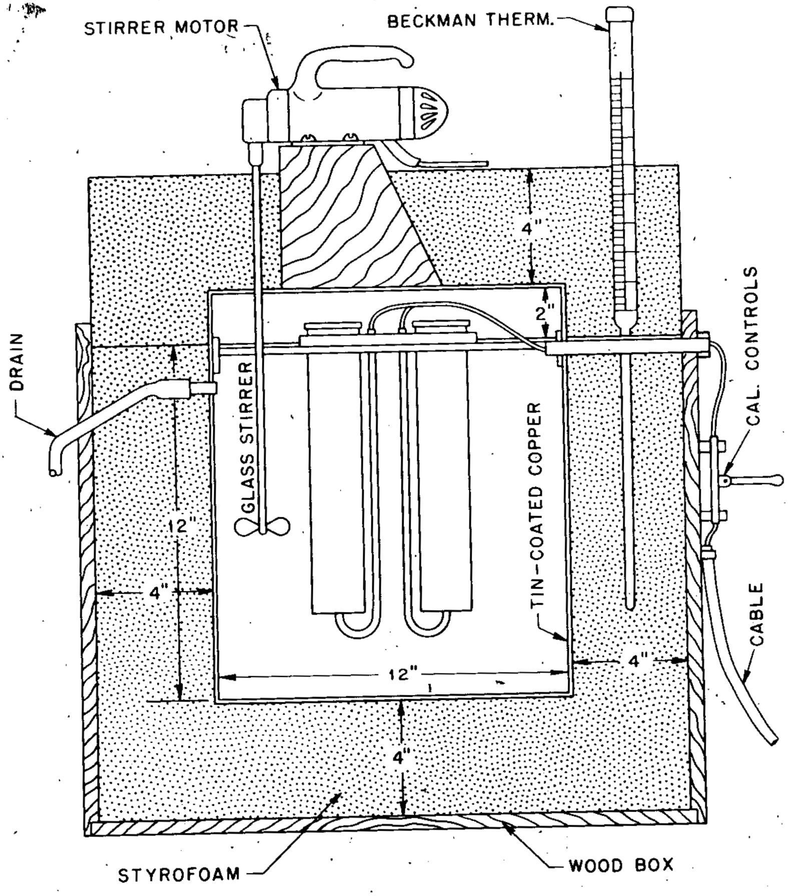
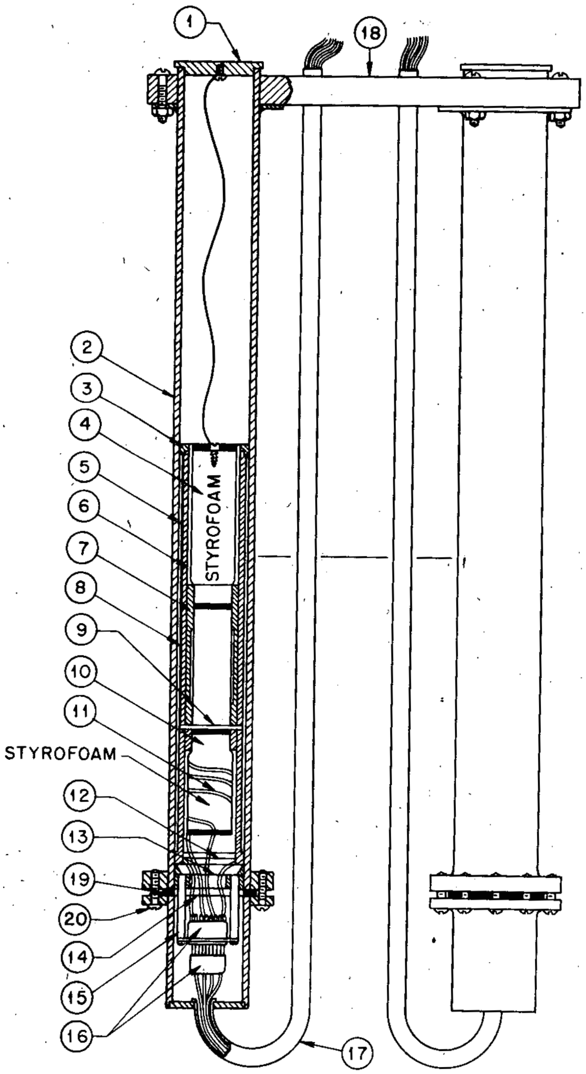


Fig. 10.7—Ice calorimeter.

Early calorimeters at Mound Laboratory had the two opposite arms of the Wheatstone bridge wound on a single form, where each arm consisted of a single layer of wire spaced by hand. In that case the inner coil operated at a slightly higher temperature than the outer coil during a measurement. At present, the coils are wound with two layers per arm and two arms per form. The outermost and innermost windings are connected in series to form one bridge arm and the two in-between



1. Cap
2. Jacket
3. Thermel support ring
4. Top baffle
5. Bridge winding
6. Thermel form
7. Heater form
8. Heater winding
9. Pin
10. Bottom baffle
11. Heater leads
12. Insulating support ring
13. Lead connector support ring
14. Bridge leads
15. Connector support pin
16. 8-point tube socket and adapter
17. Lead conduit
18. Panel
19. Gasket
20. Machine screws sufficient to complete

Fig. 10.8—Differential-bridge calorimeter assembly.

windings are connected in series to form the opposite bridge arm. The average temperature of the first and fourth windings is believed to be equal to the average temperature of the second and third windings in this arrangement. The wire is now spaced with the lead screw of a lathe instead of by hand and is wound with a more uniform tension. The use of larger wire sizes is feasible because the bridge coils are now wound a longer distance along the coil form; in fact, they are made several times the length of the sample container to minimize heat-distribution errors. The doubling of the number of layers has permitted the use of wire whose diameter is larger by the factor $\sqrt{2}$. The larger diameter wire and the more constant tension have both contributed to the attainment of more stable bridges. The more nearly equal temperature of opposite arms has furnished a more linear relation between bridge potential and sample curie value.

The speed and stability of present calorimeters have been increased over earlier models by designing sample containers to fit tightly into the calorimeter and by redesigning the heater construction so that in both cases air gaps are minimized.

Convection losses are minimized by means of Styrofoam (The Dow Chemical Co.) plugs which are mounted above and below the sample container.[25]

The forms on which calorimeter bridge coils are wound are, to a large extent, thin-wall aluminum cylinders. Formerly these forms were painted with a baking varnish to ensure no possible electrical contact between the form and the bridge coils; the present procedure is to anodize the aluminum coil form to produce a very good insulator from a chemically stable compound.[26]

6.4 *Manganin-Platinum Bridge Thermometer.* Simplification of the manner by which the bath temperature could be read resulted in the development of a manganin-platinum bridge thermometer. The usual procedure had been to read a Beckman thermometer which was immersed in the bath. It was recognized that a bridge-type thermometer could be made more sensitive than a Beckman thermometer, could have a faster response to bath-temperature changes, and could be read remotely from the bath. This bridge thermometer is described in Chap. 9, Sec. 4.7.

REFERENCES

1. P. Curie and A. Laborde, Compt. rend., 136: 673 (1903).
2. Orlo E. Myers, Nucleonics, 5: 37 (November 1949).
3. E. Rutherford and H. Robinson, Phil. Mag., 25: 314 (1913).
4. L. V. Coulter, Progress Report, Report MLM-M-1389, Sept. 1–15, 1944.
5. L. V. Coulter, Progress Report, Report MLM-M-1011, June 16–30, 1945.
6. G. R. Grove, Proposal for the Establishment of a Program of Research and Development in Calorimetry at Mound Laboratory, Report MLM-52-5-72, Apr. 23, 1952.
7. E. Rutherford and H. Robinson, Phil. Mag., 25: 312 (1913).
8. E. Rutherford and H. T. Barnes, Nature, 68: 622 (1903).
9. E. Rutherford and H. T. Barnes, Phil. Mag., 7(6): 202 (1904).

10. S. W. Watson and M. C. Henderson, Proc. Roy. Soc. London, A118: 318-334 (1928).
11. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, New York, 1947.
12. J. C. Jaeger, Phil. Mag., 32: 324-335 (1941).
13. J. M. Sturtevant, Physics, 7: 232-235 (1936).
14. J. C. Evans, Proc. Phys. Soc. London, B59: 242 (1947).
15. J. F. Eichelberger, Progress Report, Report MLM-M-342, Dec. 16–31, 1947.
16. N. Wiener, "Cybernetics," John Wiley & Sons, Inc., New York, 1948.
17. J. R. Parks, Bath Control, Stability of the Twin-bridge Calorimeter, and Thermal Noise, Report MLM-595, Aug. 15, 1951.
18. J. F. Eichelberger, Progress Report, Report MLM-118, May 1–31, 1948.
19. J. F. Eichelberger, K. C. Jordan, J. R. Parks, and W. J. Haubach, Jr., Quarterly Report for General Research, Report MLM-368-2, April, May, and June 1949, pp. 413–423.
20. K. W. Foster, F. J. Shon, E. E. Winterland, and M. N. Wolfe, Calorimetric Assay Group, Operating Manual, Report MLM-423-1, Jan. 1, 1950.
21. H. H. Fox, Recalculation of Fundamental Constants and Conversion Factors, Report MLM-960, Jan. 4, 1954.
22. J. R. Parks, Progress Report, Report MLM-350, June 1–30, 1949.
23. M. L. Curtis, Counting Technique Studies II, Discrepancy in Alpha-counting Instruments, Report MLM-373, Apr. 8, 1949.
24. J. F. Eichelberger, K. C. Jordan, S. R. Orr, and J. R. Parks, A Calorimetric Determination of the Half Life of Po^{210}, Phys. Rev., 96: 719-721 (1954).
25. J. F. Eichelberger, Progress Report, Report MLM-137, June 1–30, 1948.
26. W. J. Haubach and K. C. Jordan, Report for General Research, Report MLM-379-2, July, August, and September 1949, p. 428.

Chapter 11

WASTE DISPOSAL

By F. M. Huddleston, R. R. Deem, P. M. Hamilton,
and F. C. Mead, Jr.

1. INTRODUCTION

Information relative to the field of radioactive waste disposal has been accumulated at Mound Laboratory from the results of research, pilot-plant investigations, and $4\frac{1}{2}$ years of plant-scale operation. The plant described in this chapter was the first one of its type to be constructed for the United States Atomic Energy Commission. The activity of the process effluent is below the acceptable limits as set forth in Handbook 52 of the National Bureau of Standards.[1]

2. GENERAL DESCRIPTION OF THE PROBLEM

2.1 *Treatment of General Laboratory Wastes.* The waste-disposal problem is quite complex owing to the continuous variation in the constituents of the waste stream and to the relatively small volumes of waste solution processed. This condition is magnified by the fact that laundry wastes, chemical laboratory wastes, and wastes from radioactive decontamination all contribute to the waste stream.

Two approaches considered for possible handling of this waste are:

1. Demand of the waste-disposal unit that it act as a service facility and in no way limit scientists, craftsmen, decontamination workers, and others as to what kind of liquids may be poured into the waste stream or

2. Demand that only easily handled wastes and those of known composition be sent to the waste-treatment plant.

The approach used at Mound Laboratory is one that demands the maximum performance from the waste-disposal unit and does not restrict what may be poured down the drains, provided that the waste material will not damage the drains. Although this approach makes the disposal problem appear more difficult, it greatly reduces total cost.

All operational costs are direct costs and do not include such indirect costs as that of the scientists' time to determine what should be done with each separate waste solution.

The function of the waste unit is to strip the waste stream of sufficient radioactivity so that the process effluent will not raise the background of the river (into which this effluent is discharged) above the limits set forth in Handbook 52, National Bureau of Standards. Experiments were performed to determine the amount of radioactivity that could be discharged from the waste-disposal plant without increasing the river background. Throughout the remainder of this chapter this level of radioactivity will be referred to as "tolerance." It is also desirable for the waste-disposal plant to concentrate the activity that is removed from the waste stream to a minimum volume so that this material may be disposed of at a minimum of expense.

Table 11.1—Composition of Influent Waste

Material	Average, ppm	Maximum, ppm	Minimum, ppm
Dissolved solids	4895	7340	1295
Suspended solids	685	1811	0
Total solids	5580	9151	1295
Citric acid	39	208	0
Orthophosphate	31	52	2
Pyrophosphates	176	645	34

2.2 *Composition and Variation of Waste.* (a) *Chemical Composition.* No restrictions are made as to what material can be discharged into the collection system. Experience has shown that the following chemicals have been introduced into the waste stream in amounts varying from traces to large quantities. Some of the waste solutions contain citric acid, various detergents, chelating agents, soaps, lubricating oils, organic solvents, strong inorganic acids, sodium hydroxide, formic acid, sodium tartrate, formaldehyde, and many other substances. Most of these substances are quite concentrated at the time of entrance into the waste stream.

Analysis of 26 successive tanks containing approximately 30,000 gal each of the collected waste gave the results shown in Table 11.1 (see reference 2). The pH of these waste solutions ranged from 6.6 to 12 with an average of 9.7.

This information was adequate for the satisfactory processing of waste solutions; hence analyses for other substances were not made.

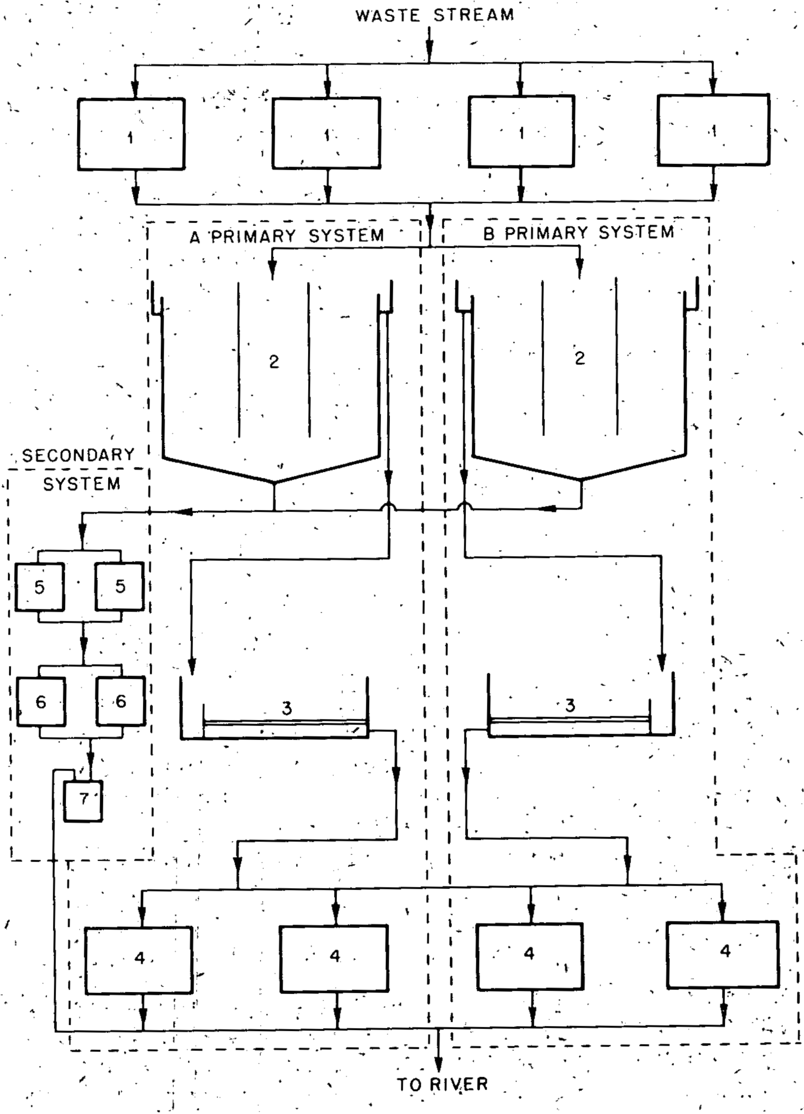


Fig. 11.1—Diagrammatical representation of waste-disposal plant.

(b) *Activity.* The waste-disposal plant (shown diagrammatically in Fig. 11.1) at Mound Laboratory receives several radioactive isotopes. The initial work was concentrated on the removal of the isotope which was considered to be the greatest hazard. In accomplishing this the other isotopes were reduced to satisfactory levels. The concentration of this activity after collection in a 30,000-gal tank was 5×10^2 to 5×10^4 times tolerance, having an average concentration of 1.4×10^3 times tolerance. These figures were obtained from 4½ years of operating data. The quantities of radioactive materials were determined by assaying samples of the waste.

A study of the waste to be processed shows that most of the activity is associated with the insoluble material; further, as shown by Table 11.2 (see reference 3), most of the radioactivity is associated with the larger size particles.

Table 11.2—Activity Associated with Particle Size

Particle size, μ	Total activity, %
Above 160	97.93
14–160	0.83
5–14	0.32
0–5	0.88

In some cases the 0- to 5-μ size has contained as much as 12 per cent of the total activity.

Experience has shown that only the portion of activity that will pass through a fine sintered-glass filter having pore openings of approximately 5 μ will not be removed by the standard process. Most of the activity which will pass through such a filter is in the colloidal state or in solution. Filtration of a sample of the influent is used as a control method for pretreatment prior to the introduction of each tank of waste into the standard process.

3. LIQUID-WASTE PROCESS

3.1 *Collection of Waste.* The waste-collection system is composed of waste lines from the laundry and from floor drains, showers, lavatories, janitorial sinks, and laboratory sinks in the Biological Research Building, the General Research Building, and various other laboratories. In most cases the waste lines are standard bell and spigot Duriron pipe, vitreous clay pipe, standard schedule 40 steel pipe, or cast-iron soil pipe. The waste lines from each building are underground, and the flow is normally by gravity past conventional manholes. Sumps and automatically controlled pumps are used to move the waste where gravity flow is not possible. All the lines join together in one 8-in. line that enters the Waste Disposal Building through a concrete tunnel. Inside the building the line branches into four influent tanks (item 1, Fig. 11.1) having hopper-shaped bottoms. Each branch is provided with a valve in order that the waste can be diverted into any tank. These tanks are constructed of steel-lined concrete and have a capacity of 30,000 gal each. Each tank is equipped with two side-entering agitators, a hydrostatic-pressure-type level indicator, and a high-level alarm. The tanks are totally enclosed and have overflow lines which connect to the adjoining tanks. It is common practice to fill one tank at a time and process the contents as soon as possible.

3.2 *Preliminary Treatment of Liquid Waste.* When an influent tank has been filled to the desired level, it is shut off from the system to prevent additional waste from entering. Owing to the wide variation in the characteristics of the solution from tank to tank, a pretreatment is required to reduce adverse effects of these variations.

The purpose of the pretreatment is to bring about coprecipitation with and adsorption of the activity on particulate matter that can be removed by the standard process.

Filtration of a sample of the waste solution through a fine sintered-glass filter is the method employed to determine the kind and extent of pretreatment required. Operational experience has shown that the filtrate of such samples must not contain more than 50 per cent of tolerance if a satisfactory end product from the waste-disposal process is to be obtained. Using this tolerance as a guide, many detailed studies were made in the laboratory. Reagents used for these experiments were ferrous sulfate, ferric chloride, sodium sulfide, calcium chloride, barium chloride, activated carbon, aluminum sulfate, and many others. After many tests and pilot-plant runs, it was found that a pretreatment using various combinations of calcium chloride, barium chloride, sodium sulfide, aluminum sulfate, and activated carbon (Aqua Nuchar) would meet the rigid requirements in all cases. Calcium chloride will precipitate the ortho-acid pyrophosphates. Barium chloride is an excellent scavenging agent and will precipitate both anions and cations under certain conditions. Sodium sulfide will form sulfide and hydroxide precipitates. Aluminum sulfate forms a floc in the clariflocculator which acts as a scavenging agent. The activated carbon is an adsorption agent which adsorbs small particles and many organic substances.

The following pretreatment is effective in most cases:

1. The influent tank is shut off from the system when full (approximately 30,000 gal).
2. Agitation of the tank contents is begun and is continued until the solution is ready for processing through the standard process.
3. The pH of the solution is adjusted to between 6 and 8 with 66°B sulfuric acid.
4. Activated carbon, 48 lb, is added in the form of a slurry.

5. Sodium sulfide, 6 lb, is added in the form of a 20 per cent aqueous solution.

6. Calcium chloride of commercial grade, 150 lb dry weight, is added in the form of an aqueous solution.

7. A contact time of approximately 30 min with agitation is allowed.

A sample of the pretreated waste is taken to the laboratory, and the pH of the sample is adjusted to 8.8 with sodium hydroxide. The sample is then filtered through a fine-porosity sintered-glass filter. The filtrate is assayed to determine the concentration of activity. If the filtrate is within tolerance, the tank is ready to be discharged to the standard process. In most cases this pretreatment is sufficient to reduce the concentration of activity to below tolerance. However, in a few cases multiple pretreatments are necessary using the same reagents and using barium chloride and aluminum sulfate as additional reagents. The exact amount of each reagent used in the multiple treatments is determined in the laboratory prior to plant-scale treatment.

3.3 *Coagulation and Sedimentation of Particulate Matter.* The waste-disposal process uses two standard clariflocculators (item 2, Fig. 11.1) manufactured by the Dorr Co., Chicago, Ill. Each consists of a flocculator and clarifier. The clarifier is 30 ft in diameter, has a cone-shaped bottom, and has a side depth of 10 ft. The flocculator is located in the center of the clarifier and is 16 ft in diameter with a side depth of $7\frac{1}{2}$ ft. The flocculator is equipped with a rotating-blade agitator that turns at 2 rpm. The clarifier is equipped with plows in the bottom to move the sludge toward the apex of the cone-shaped bottom. Sludge is withdrawn from the center of the cone-shaped bottom of the clarifier. The plows are turned at 0.05 rpm. Figure 11.2 shows one of the clariflocculators installed in the Waste Disposal Building.

The clariflocculators are equipped with pH controllers and recorders (Leeds & Northrup Company, Philadelphia, Pa.) which utilize standard immersion-type cells.

The pretreated waste enters the mix trough of the clariflocculator through suitable flowmeters. At this point aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] is added at the rate of 10 grains per gallon of influent. The pH is adjusted to and controlled at 8.8 with a 5 per cent solution of sodium hydroxide.

The sludge collects and concentrates in the bottom of the clariflocculator. The concentration is such that the average sludge withdrawn is 12 to 18 per cent solids and contains practically all the radioactivity. At all times a sludge blanket is maintained to a depth of approximately 6 in. below the bottom of the flocculating chamber. Sludge is withdrawn at a rate that maintains this blanket at a constant depth. Retention time for sludge in the clariflocculator is from 4 to 8 months. Plant-scale tests have been made with various sludge levels and with no sludge at

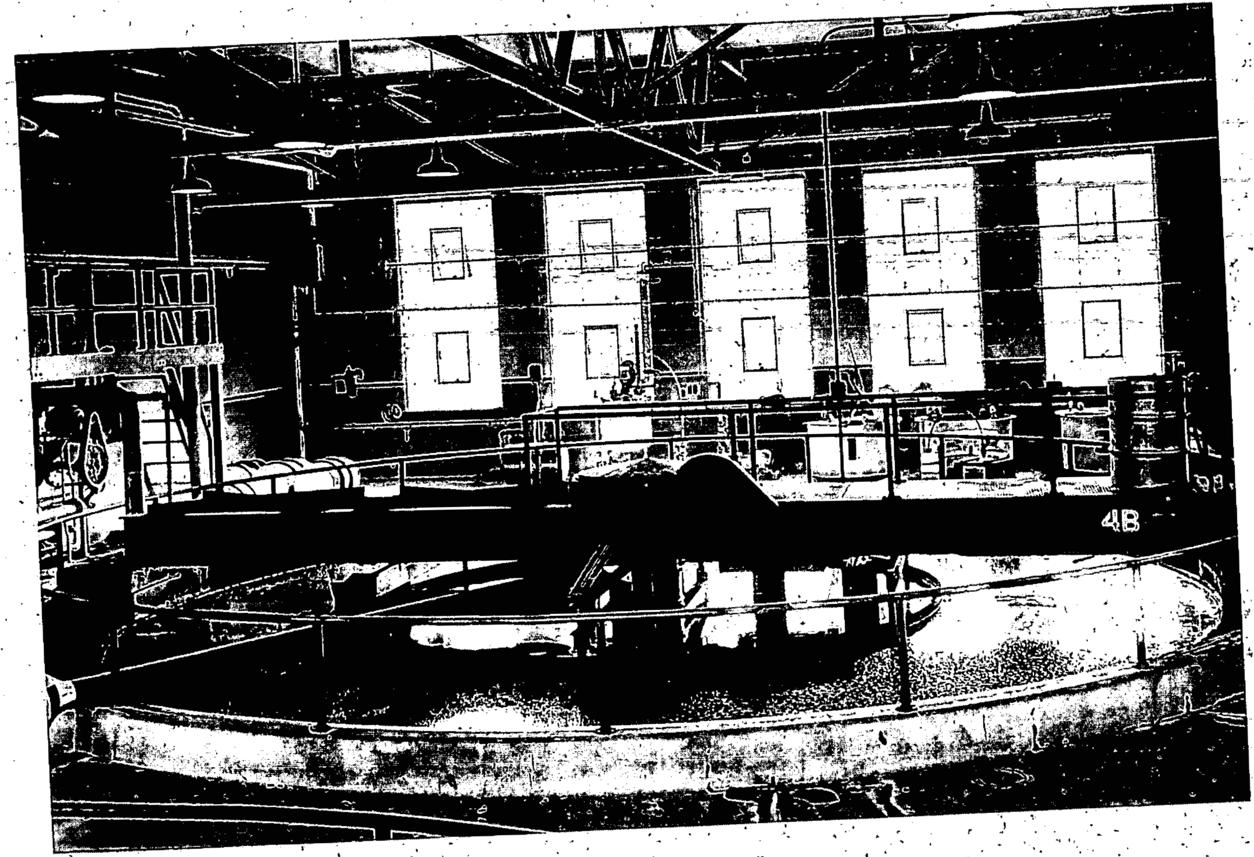


Fig. 11.2—Clariflocculator installation.

all. There is no doubt that the sludge blanket is necessary in order to obtain optimum results.

Close observation of the sludge blanket indicates that the sludge level increases or decreases during intervals as short as 2 hr. In addition to expansion and contraction, mountains, valleys, and islands of sludge have been observed at various times. Numerous attempts have been made to measure the blanket height, using photoelectric cells and electric lights. The best method to locate the sludge-supernatant interface is that of uncapping a bottle immersed in the solution at various depths. It has been found that the sludge is almost a homogeneous mixture, after a lag time of about 2 days, due to agitation provided by the sludge plows. However, sometimes the sludge blanket becomes upset, and it requires several days for the sludge bed to stabilize and the clariflocculator to return to normal operating condition. Upsets can be caused by improperly pretreated influent, radical pH changes, or rapid agitation of the sludge.

No attempt is made to destroy bacteria in the sludge. In fact, bacteria appear to be beneficial to the operation of the process since it is believed that they destroy part of the polonium citrate complexes from laundry wastes. Citrate destruction has been established by analysis for citrates in the clariflocculator feed and effluent. The formation of hydrogen sulfide by the bacteria is also thought to be beneficial. Analysis of gases formed during processing indicates that both carbon dioxide and hydrogen sulfide are present. A large portion of the generated gas is removed by the gentle agitation caused by the plows. Most of the remaining gas can be liberated by recirculation with centrifugal pumps. However, this type of agitation is detrimental in that poor settling results from breakage of the floc. The residual gas is not of sufficient quantity to cause buoyancy of the sludge; hence complete removal is unnecessary. Typical bacteria counts in the sludge are tabulated in Table 11.3 (see reference 4).

3.4 *Final Treatment and Filtration.* (a) *Use of Acid-Carbon and pH Change.* The supernatant solution from the clariflocculators varies in carry-over of insolubles from about 2 to 65 ppm. This is due to variations in clariflocculator feed and due to intermittent operation of the equipment. Precipitation of aluminum in the clariflocculator was found to be incomplete at a pH of 8.8. The most recent process improvements have been made by improving clariflocculator effluent.[5]

Some difficulty was encountered in the filtration of the clariflocculator overflow. The acid-carbon system was installed to overcome this trouble. Addition of acid-activated carbon aids in the reduction of the aluminum complexes in the carry-over and reduces the effect of variation of insolubles in the carry-over. A slurry of activated carbon (Aqua Nuchar) in 1N sulfuric acid in sufficient quantity to adjust the pH from

8.8 to 6.0 is added to the clariflocculator effluent. This process, employing inadequate equipment, has been in use for about 2 years and has produced excellent results. The installation of proper equipment should give even better results.

During the 2 years of operation with the manually controlled carbon-acid addition, smaller amounts of other reagents have been used. Also, multiple pretreatments have been almost completely eliminated. The acid-carbon acts as an excellent adsorbent and forms a center for floc formation. The pH change results in the formation of aluminum floc from the aluminum remaining in solution after the incomplete precipitation of aluminum in the clariflocculator. The optimum amount of carbon is about 125 ppm.

Table 11.3 — Total Bacteria in Clariflocculator Sludge†

Clariflocculator A, no./ml	Clariflocculator B, no./ml
3.0×10^7	1.45×10^7
1.5×10^7	4.5×10^7
7.8×10^6	1.05×10^7
7.0×10^5	4.0×10^5
1.6×10^6	3.2×10^6
2.5×10^6	5.9×10^5

†Bacteria samples were taken weekly for 6 weeks.

(b) *Sand Filter Operation.* Two rapid sand filters (item 3, Fig. 11.1), standard units manufactured by the Hardinge Company, Inc., York, Pa., are used to filter the treated clariflocculator effluent. These units are equipped with automatic or manual control for backwash and sand-cleaning operations. The filters are 12 ft wide and 24 ft long. Each filter consists of supports, 36 sections with porous plates, sand, and effluent piping. One of these filters is shown in Fig. 11.3.

The filters are loaded with sand to a depth of about 10 in. The sand is furnished by the Delhi Foundry Sand Co., Cincinnati, Ohio, and is a silica sand with an effective size of 0.147 mm with a uniformity coefficient of 1.4.

The filters are backwashed, only when required, to maintain a satisfactory filtration rate. Filter effluent water is used for the backwash, and the volume used averages 3.5 per cent of the volume filtered. The backwash rate is about 12 gal/min per square foot of filter area. The backwash water is recycled back to the influent tanks for reprocessing.

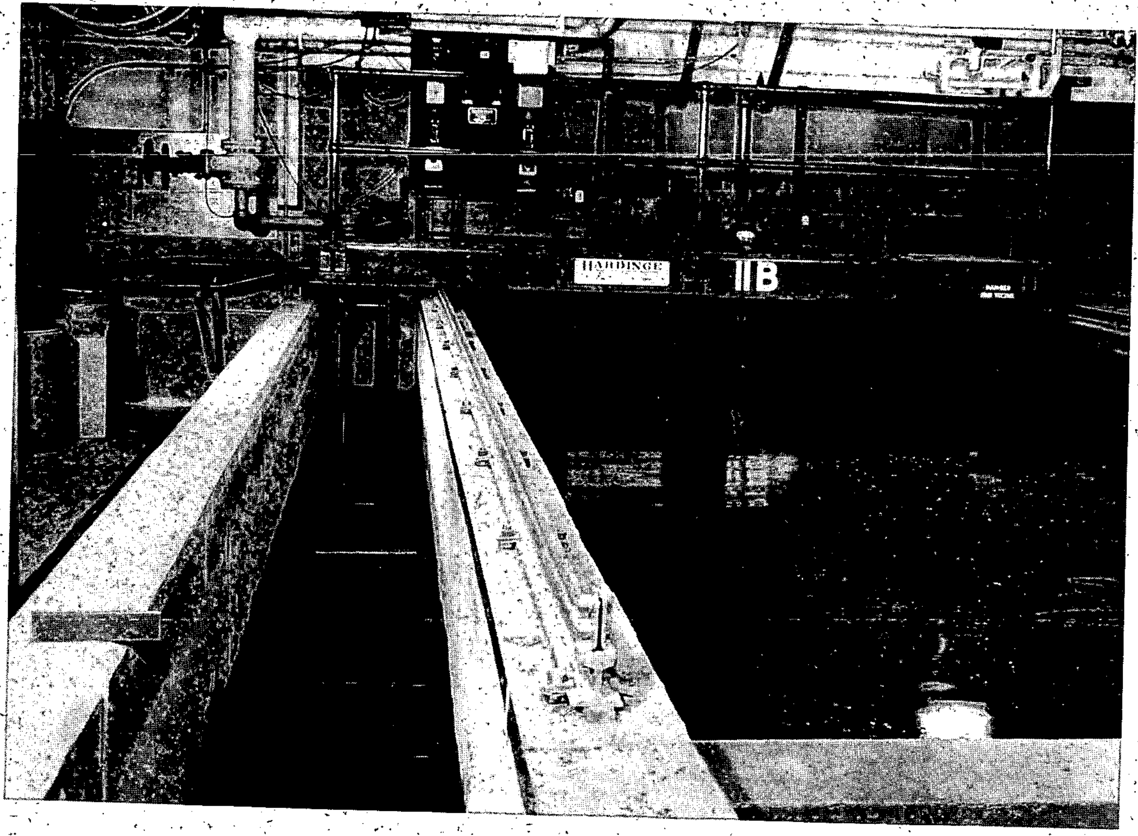


Fig. 11.3—Sand filter installation.

The filters operate with a head of 0 to 24 in. The normal rate of filtration is approximately 0.27 gal/min per square foot of filter area.

Although some evidence of growth of sand particles has been observed,[6] no trouble has been encountered by such growth. This growth seems to be very slow at pH 6.0. Operational experience indicates that the sand can be used indefinitely. Replacement of sand that is lost owing to washout during backwash is about 3 per cent per year.

The use of the acid-carbon and maintenance of the waste solution at pH 6.0 aids in the formation of the schmutzdecke[7] (carbon sludge blanket) on top of the sand. Very little penetration is observed, even to a depth of 1 in. This schmutzdecke serves as an excellent filter medium and acts as a good adsorbent medium.

Although some channeling has been encountered, it can be corrected by backwashing. "Mud balling" was a fairly serious problem when the sand filters were fed with waste solution at pH 8.8. However, no mud balling is encountered at pH 6.0. Intermittent operation impairs the filter efficiency slightly. Expansion and contraction of the schmutzdecke have been observed, but they do not cause trouble.

3.5 *Final Effluent.* The filtrate from the sand filters is collected in four rectangular, concrete effluent tanks (item 4, Fig. 11.1) having a capacity of 30,000 gal each. Each tank is equipped with a side-entering agitator, a liquid-level indicator, and a high- and low-level alarm system. When a tank is filled, the contents are agitated and then sampled. The sample is assayed to determine the concentration of activity. The average concentration of activity for 4½ years of operation has been 79 per cent of tolerance. The lowest monthly average has been 7 per cent of tolerance, and the lowest result on an individual tank of 30,000 gal has been less than 1 per cent of tolerance. The operational summary is shown in Table 11.4.

Decontamination factors greater than those described here are possible, but the added expense required to attain such factors is unwarranted, since the method described will produce an effluent well below present tolerances. The average decontamination factor has been 1.7×10^3, although factors as high as 1.0×10^6 have been attained in plant-scale operations.

After assay of the effluent is made, and if the effluent is below tolerance, the tank contents are discharged into the river. Less than 0.5 per cent of the effluent is recycled.

4. SOLID-WASTE PROCESS

The sludge formed in the clariflocculators is withdrawn periodically and is moved with an Oliver diaphragm slurry pump (Oliver United Filters, Inc., Chicago, Ill.) to 1000-gal sludge-holding tanks (item 5,

Fig. 11.1). From these storage tanks the sludge is pumped to 100-gal glass-lined reaction vessels (item 6, Fig. 11.1) with automatically controlled Oliver diaphragm pumps that cut off when a predetermined level is reached in each vessel. Usually the volume is 60 gal, but this can be varied to allow for process control. Two gallons of 66°B sulfuric acid is added to the sludge at a rate such that approximately 15 min is required to complete the addition. The resultant pH is approximately 2.5, and, in the sludge at this pH, aluminum, calcium, and iron go into solution, and carbon dioxide and hydrogen sulfide are liberated. A small amount of radioactivity is leached from the sludge in this operation. During addition of the acid, mechanical agitation is used, and the evolved gases are passed through a filter system to remove particulate matter. The acidified sludge is then fed by gravity to the final filtration apparatus.

Table 11.4 — Summary of Waste-disposal Operations

Period	Radioactivity concentration, × tolerance: Influent	Radioactivity concentration, × tolerance: Effluent	Decontamination factor
Jan. 1949–July 1949	828	0.16	5,175
July 1949–Jan. 1950	1,290	1.03†	1,252
Jan. 1950–July 1950	946	1.72†	550
July 1950–Jan. 1951	1,017	3.61†	281
Jan. 1951–July 1951	828	0.28	2,957
July 1951–Jan. 1952	1,420	0.28	5,071
Jan. 1952–July 1952	1,180	0.28	4,214
July 1952–Jan. 1953	2,040	0.12	17,000
Jan. 1953–July 1953	544	0.20	2,720

† Dilution water was used during these periods to adjust the waste-disposal-plant effluent to tolerance level.

The acid slurry flows into 30-gal, polyethylene-lined, open-head drums (item 7, Fig. 11.1) and is maintained at a constant level in these drums. The filtrate is continuously withdrawn from the slurry, by vacuum, through Moore-type filters[8] (Fig. 11.4) which are immersed in the drum. Since the insolubles contained in the slurry are more than 90 per cent carbon, the slurry filters quite rapidly and maintains an open lattice. Filtration of the slurry continues until the drum contains a solid cake, at which time the filter is withdrawn and the drum is capped and removed for burial. Solid-cake thicknesses exceeding 6 in. may be formed by use of this system. The drum contains approximately 27 gal

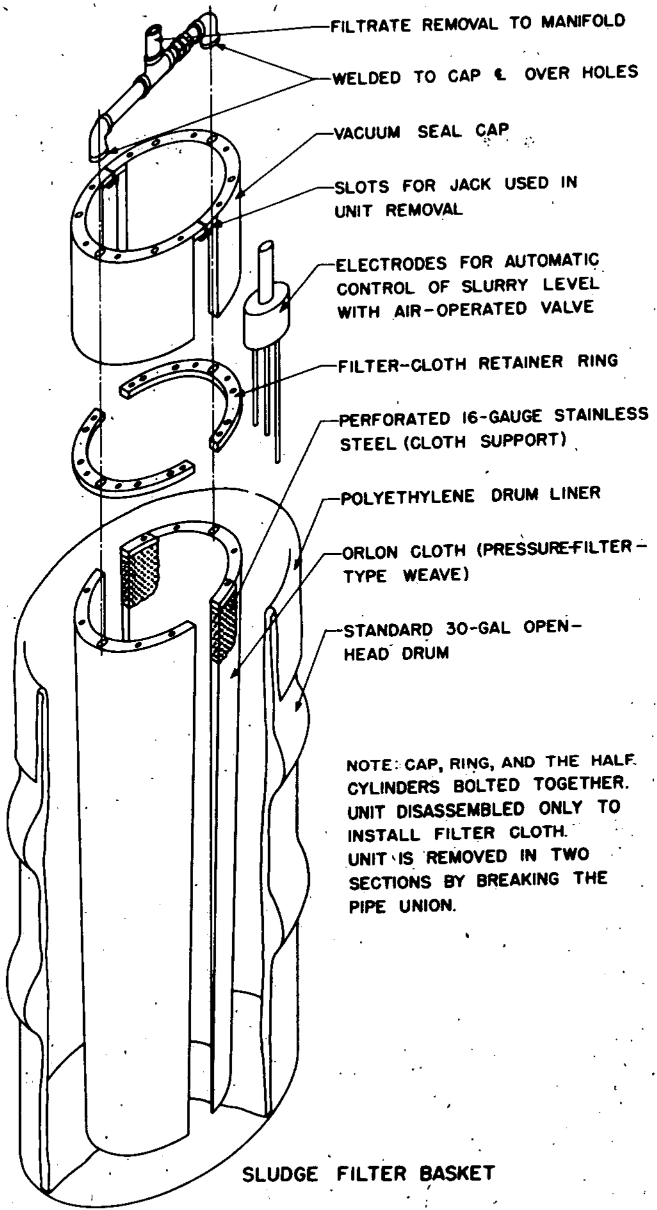


Fig. 11.4 — Moore-type filter.

of solid cake which is about 40 per cent solids and with an activity concentration about equal to that contained in a 30,000-gal influent tank. Attempts to further reduce the residual volume by freezing or incineration were not successful.

The volume reduction of the entire waste process for the past 4½ years was greater than 700 to 1. However, the volume reduction for the past 2 years has been 625 to 1. A slightly increased volume reduction should be possible if proper equipment for the addition of activated carbon is installed because of the reduced volume of reagents which would then be required.

The filtrate from this final filtration is corrosive and is handled in Haveg (Haveg Corporation, Newark, Del.) tanks and lines. This solution has a soluble salt content of 4 to 9 per cent and a volume equal to $^1/_{300}$ of that obtained from the sand filter effluent. The average concentration of activity is the tolerance level for effluent to the river. After approximately 100 gal of this filtrate is collected, it is assayed to determine the concentration of activity. If the activity level is below tolerance, the liquor is discharged to the river along with 30,000 gal of the sand filter effluent.

5. PLANT MAINTENANCE

5.1 *Tanks, Clariflocculators, and Lines.* The steel tanks and clariflocculators require very little maintenance other than painting. A painting schedule has been started whereby most surfaces are recoated at about 3½- to 5-year intervals. Inspections have shown this schedule to be adequate. The waste lines at Mound Laboratory require practically no maintenance.

Normal maintenance of the pumps is required, and, because some of these are of the closed-impeller type, cleaning is necessary on those handling the feed to the clariflocculators. Mop strings, lint, animal hair, and other substances must be removed from the pumps at intervals of about 3 weeks.

5.2 *Sand Filters.* The sand filters require surface washing with a fire hose about once each year to aid in maintaining clean sand. Some evidence of corrosion has been observed which is probably due to improper pH control during experimental runs. Replacement of five of the 36 porous plates in one filter was necessary. The filter replacement resulted from insufficient backwashing and because the unit had not been used for some time. During the time that the filter was not in use, algae formed within the plates and completely blocked them. In normal use, and with proper care, this trouble is not encountered.

5.3 *General Maintenance.* Experience shows that slight additional time and cost are required to maintain this plant compared to the time and cost needed to maintain a municipal water-treatment plant.

6. HYDROLYSIS OPERATIONS[9]

The waste hydrochloric acid solution containing the dissolved bismuth slugs from which the polonium has been separated contains a very high concentration of bismuth, an average of about 300 g of bismuth per liter of solution. It is desirable to remove this bismuth from the solution before the solution enters the stream which receives the standard waste-disposal treatment.

The hydrochloric acid is pumped into a hydrolysis tank where it is neutralized and hydrolyzed by the addition of sodium hydroxide solution. The solution is thoroughly agitated during this operation, and the pH is continually checked. The final pH of the solution is about 12. The bismuth precipitates as bismuth oxychloride. The slurry of solution and bismuth oxychloride flows into an Eimco rotary-drum filter (The Eimco Corp., New York) which separates the precipitate and filtrate. The filtrate then enters the stream which receives the standard waste-disposal treatment.

The filtered bismuth oxychloride drops from the filter into a 30-gal drum for disposal. A process has been developed (Chap. 7, Sec. 13) whereby this bismuth can be recovered for reuse.

7. COST OF OPERATION

The cost of operating the Mound Laboratory waste-disposal plant (excluding hydrolysis operations) includes research, process improvement, supervision, labor, chemicals, power, maintenance, overhead, plant investment, and depreciation. The investment is written off at 10 per cent per year for process equipment and at 2 per cent per year for the building of rugged reinforced-concrete construction. Over-all cost is $14,300 per million gallons of effluent. This figure is roughly 10 per cent of the cost of evaporation, which runs as high as $130,000 per million gallons, but it is much higher than the average municipal water-treatment cost of $50 per million gallons.[10]

Several factors make the cost per gallon of waste processed many times greater than the cost for municipal water treatment. These factors are as follows:

1. Mound Laboratory operates 8 hr per day compared to a 24-hr day at water plants.
2. The influent waste varies so much in composition that multiple pretreatment is sometimes necessary.

3. All waste, liquid or solid, must be carefully assayed and handled to ensure health and safety of the operators as well as of the public.

4. Much more waste could be processed by the present staff and equipment, which would lower the cost per unit volume.

5. Many reagents are used in relatively large quantities to ensure proper handling and disposal of the water.

6. Several corrosive reagents uncommon to the water industry are used, causing materials and maintenance to be more costly.

REFERENCES

1. National Bureau of Standards Handbook 52, Mar. 20, 1953.
2. P. M. Hamilton, H. J. Morris, and R. L. Norton, Quarterly Report for General Research, Report MLM-405-2, October, November, and December 1949, p. 123.
3. R. L. Norton, Report for General Research, Report MLM-535, Oct. 30, 1950, to Jan. 22, 1951, p. 32.
4. P. M. Hamilton, F. M. Huddleston, H. J. Morris, R. L. Norton, and G. D. Stewart, Report for General Research, Report MLM-379-2, July, August, and September 1949, p. 291.
5. R. R. Deem, Improvements on Primary System, Liquid-waste-disposal Process, Report MLM-762, Aug. 26, 1953.
6. J. R. Baylis, J. New Engl. Water Works Assoc., 51: 1-36 (1937).
7. W. J. Ryan, "Water Treatment and Purification," 2d ed., p. 33, McGraw-Hill Book Company, Inc., New York, 1946.
8. H. E. Feierstein and R. R. Deem, Improvements on Secondary System, Liquid-waste-disposal Process, Report MLM-555, May 15, 1951.
9. J. R. Grice, Operations Manual for Hydrolysis Group, Report MLM-389, Oct. 12, 1949.
10. C. C. Ruchhoft, A. E. Gorman, and C. W. Christenson, Ind. Eng. Chem., 44: 549 (1952).

Chapter 12

NEUTRON SOURCES AND ALPHA SOURCES

By John L. Richmond

1. NEUTRON SOURCES

1.1 *Introduction.* The neutron has played an increasingly important role in nuclear physics since its discovery by Chadwick in 1932. One can follow the history of the neutron by consulting texts on nuclear physics[1–3] and by referring to the work of some of the many contributors to the science of the neutron, such as Fermi, Bethe, Goldhaber, Alvarez, and Joliot.

Because the properties and reactions of neutrons can be readily found in the literature, they will be summarized and a lengthy discussion omitted.

The neutron has an atomic weight of 1.00897, mass of 1.67×10^{-24} g, magnetic moment of -1.913 magnetons, wavelength of about 1 A in the thermal region (0.038 ev), and a velocity of 2.2×10^5 cm/sec in the thermal region, and 1.4×10^9 cm/sec at 1 Mev.

Since the neutron has no charge, it is rather unreactive. Its absorption cross section is quite low, with the exception of resonance capture of thermal neutrons by such elements as boron, cadmium, and indium. A neutron loses its energy by collisions with nuclei. A neutron of 1 Mev is thermalized by about 18, 90, and 114 collisions with hydrogen, beryllium, and carbon, respectively. When the neutron is captured, a gamma, neutron, proton, deuteron, or alpha is usually emitted from the compound nucleus.

1.2 *Sources of Neutrons.* Neutrons are produced by the nuclear reactions (α,n), (γ,n), (d,n), and (p,n) and by fission. There are no radioactive neutron emitters. Alphas, deuterons, and protons can be accelerated to the energies required for neutron-emitting reactions. Accelerators are used chiefly for producing very high energy neutrons and monoenergetic neutrons as in the reactions $_3Li^7(p,n)_4Be^7$, $_4Be^9(d,n)_5B^{10}$, $_3Li^7(d,n)_4Be^8$, and $_1H^3(\alpha,n)_3Li^6$. Production of neutrons by accelerators is limited to the time the accelerator is in operation, whereas radioactive materials mixed with certain target elements offer a continuous source of neutrons.

1.3 *Gamma-Neutron Reactions.* Gamma rays impinging on beryllium can produce neutrons if the energy is above the (γ,n) threshold energy of 1.63 Mev. Some elements used in photoneutron sources are Na^{24}, Mn^{56}, Ga^{72}, Y^{88}, Sb^{124}, and La^{140}. Photoneutrons are essentially monoenergetic with the energy of the incident gamma less the threshold and nucleus recoil energies. By picking a variety of gamma emitters, monoenergetic neutrons are obtained at various levels.

Photo sources are limited in usefulness by the low (γ,n) cross section. They are usually fabricated at the place of use by inserting a gamma source into a well in a block of beryllium.

1.4 *Alpha-Neutron Reactions.* Alpha particles react with nuclei of atoms to produce neutrons. The alpha particle has a charge of +2 and can penetrate the nucleus of an atom if it has sufficient energy to overcome the coulomb repulsion of that atom. Alphas from radioactive elements usually cannot penetrate the coulomb repulsions of atoms heavier than argon; however, a few particles do enter the nuclei of elements heavier than argon by a process termed "leaking through the potential barrier."[1]

The neutron yield of a given element increases with alpha energy. This relation is reported graphically by Anderson.[4] For alphas of 3, 4, 5, and 5.3 Mev on beryllium, the respective neutron yields are 12, 26, 61, and 77 neutrons per 10^6 alphas.

Alpha-neutron reaction energies are positive, as for beryllium and boron, or negative, as for lithium and fluorine. It is possible for a neutron to be emitted with the energy of the incoming alpha plus the reaction energy, except for the small recoil energy of the resulting nucleus. In many cases the resulting nucleus is left in an excited state and emits a gamma on return to the ground state. This gamma energy is not available to the neutron.

Reaction energies, coulomb repulsions, and neutron yields are summarized in Table 12.1. Reaction energies are based on atomic weights as given by Friedlander and Kennedy.[2] Neutron yields are based on data of Roberts as reported by Anderson.[4] The neutron yields given in Table 12.1 are for complete absorption of alphas in the target element (thick target yield).

If several elements are combined, the neutron yield of each element is calculated from a formula given by Wattenberg, as cited by Leitz.[5]

$$N_i(\text{mix}) = \frac{F_i A_i^{-1/2} N_i(\text{pure})}{\sum_i F_i A_i^{-1/2}}$$

where N_i(pure) = neutron yield of pure element i
N_i(mix) = neutron yield of element i in mixed target
F_i = weight per cent of element i in mixed target
A_i = atomic weight of element i

The formula has been proved approximately correct by preparing mixed target sources which yielded 90 per cent of the neutrons calculated by the formula. The neutron yield of sources prepared from pure elements seldom exceeds 90 per cent of theoretical (see Table 12.1).

Since the largest neutron yields are from beryllium, boron, and fluorine, these elements are most commonly used in neutron sources. Fluorine must be in combination and is generally used as sodium fluoborate.

Table 12.1—Energy Balances and Neutron Yields of Alpha-Neutron Reactions

Isotope	Abundance, %	Reaction energy Q, Mev	Coulomb repulsion, Mev	Neutrons per 10^6 alphas of Po	Neutrons/sec per curie of Po
H^3		−4.65	0.63		
He^4	100	−18.90	1.20		
He^6		0.77	1.13		
Li^6	7.30			2.7	1.0×10^5
Li^7	92.70	−2.79	1.64		
Li^8		6.65	1.60		
Be^7		−6.41	2.20		
Be^8		−11.25	2.15		
Be^9	100	5.74	2.10	77	2.85×10^6
Be^{10}		3.86	2.05		
B^{10}	18.83	1.37	2.57	22	8.14×10^5
B^{11}	81.17	0.27	2.52		
C^{12}	98.9	−8.40	2.97	0.10	3.7×10^3
C^{13}	1.1	2.36	2.92		
C^{14}		−1.74	2.87		
N^{14}	99.62	−4.68	3.36	0.01	3.7×10^2
N^{15}	0.38	−1.96	3.31		
N^{16}		0.43	3.26		
O^{16}	99.757	−11.96	3.74	0.07	2.6×10^3
O^{17}	0.039	0.64	3.69		
O^{18}	0.204	0.21	3.64		
O^{19}		4.86	3.59		
F^{18}		−1.90	4.10		
F^{19}	100	−1.90	4.05	12	4.44×10^5

Table 12.1 — (Continued)

Isotope	Abundance, %	Reaction energy Q, Mev	Coulomb repulsion, Mev	Neutrons per 10^6 alphas of Po	Neutrons/sec per curie of Po
Ne^{20}	90.51	−6.02	4.45		
Ne^{21}	0.28	1.96	4.40		
Ne^{22}	9.21	−0.37	4.35		
Ne^{23}		6.79	4.30		
Na^{22}		−1.53	4.82		
Na^{23}	100	−1.64	4.77	1.5	5.55×10^4
Na^{24}		2.48	4.72		
Na^{25}		1.27	4.67		
Mg^{24}	78.60	−6.93	5.15	1.4	5.18×10^4
Mg^{25}	10.11	2.01			
Mg^{26}	11.29	−1.71			
Mg^{27}		3.97			
Al^{26}		−3.76			
Al^{27}	100	−2.27	5.43	0.74	2.74×10^4
Al^{28}		1.36			
Al^{29}		1.65			
Si^{28}	92.28	−7.76	5.80	0.16	5.92×10^3
Si^{29}	4.67	0.62			
Si^{30}	3.05	−1.71			
Si^{31}		3.78			
P^{30}		−3.48			
P^{31}	100	1.92	6.12	0.02	7.4×10^2
P^{32}		−1.14			
P^{34}		0.06			
S^{32}	95.1	−8.52	6.45	0.02	7.4×10^2
S^{33}	0.74	−2.83			
S^{34}	4.2	−5.25			
S^{35}		−0.20			
S^{37}		1.36			
Cl^{34}		−4.88			
Cl^{35}	75.4	−5.46	6.73	0.011	4.07×10^3
Cl^{36}		−0.88			
Cl^{37}	24.6	−3.30			
Cl^{38}		1.82			
A^{37}		−2.46			
A^{40}	99.57	−1.62	6.90	0.38	1.41×10^4

1.5 *Neutron Sources from Radium and Polonium*. Radium and polonium are used principally as the alpha emitters in the preparation of neutron sources. Radium has the advantage of a long half life (1620 years), which gives sources of nearly constant neutron emission. However, the gamma radiation from radium is much greater than from polonium. The short half life of polonium (138.40 days) means a small amount of material per curie and therefore little self-absorption of alphas.

Radium-beryllium and small polonium-beryllium neutron sources are supplied by the Eldorado Mining Company of Canada. Neutron sources from polonium and any of the target elements listed in Table 12.1 are supplied by Mound Laboratory. Neutron sources can be supplied which emit neutron fluxes of greater than 10^6 neutrons/sec.

1.6 *Methods of Preparing Neutron Sources*. The alpha emitter must be intimately mixed with the target element[6] to obtain a high neutron yield. The importance of distribution is shown by the fact that the path of a polonium alpha of 5.3 Mev is only about 0.0018 cm in polonium or beryllium.

Radium-beryllium neutron sources are made by evaporating to dryness a solution of radium bromide on beryllium powder. The mixture is solder-sealed in a brass capsule to prevent loss of radon. The method is simple, but the bromine is a diluent which reduces neutron yield.

Neutron sources from polonium were made at the Dayton Project for the first time in 1945. Polonium production at that time was in minute quantities; hence the sources were quite small. When bismuth was irradiated in a reactor, production of polonium in quantity became possible. The preparation of neutron sources in quantity was then developed according to the methods suitable for each type.

1.7 *Polonium-Beryllium Neutron Sources*. The first polonium-beryllium neutron sources made at the Dayton Project were made by plating polonium on platinum or beryllium disks and sandwiching these between beryllium disks.[7] The efficiencies were low with the small amounts of polonium used; therefore the technique showed no promise for large sources.

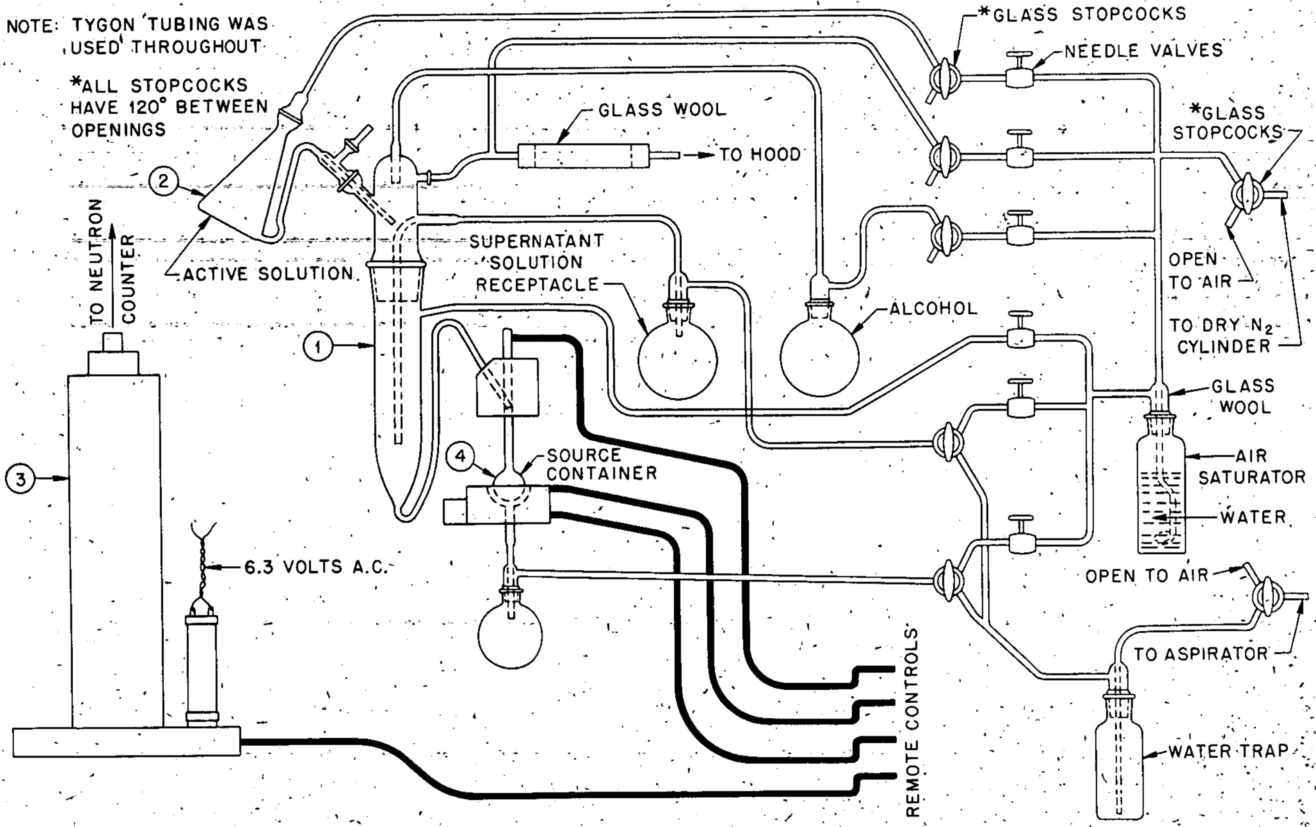
Polonium is quite low in the electromotive series of elements and will electrochemically deposit on the light metals. This principle was used for several years in the preparation of polonium-beryllium neutron sources. At first, beryllium was either shaken or stirred in a 1.5N nitric acid–polonium solution for several hours. The length of shaking time was determined by sampling the solution and taking alpha counts until 90 per cent or more of the polonium was deposited. The acid solution was then decanted, and the powder was washed with alcohol, dried, and transferred to a metal container.[8] To make large sources by this method, the reduction and deposition of the polonium was done in steps, and the portions of powder were combined in one container.

The last beryllium sources made by this method were made in a semiremote-controlled apparatus,[9] which is shown schematically in Fig. 12.1. Beryllium powder of 230 to 325 mesh was stirred in chamber 1 (Fig. 12.1) with a stream of nitrogen in 1.5N to 3.0N nitric acid. The higher concentration of acid was used only to hold larger quantities of polonium in solution (chamber 2). The deposition time in 3N acid was made as short as possible because of the increased solubility of beryllium. Deposition times in this apparatus were usually less than 1 hr. Completion of the deposition was determined by a neutron probe (No. 3, Fig. 12.1) attached to a ratemeter. When the neutron emission reached a maximum, the acid solution was drawn off through a sintered-glass filter. The powder was rinsed with alcohol and transferred as a slurry in alcohol to a container with an Oilite (The Amplex Mfg. Co., Sub. of Chrysler Corp., Detroit, Mich.) filter (No. 4, Fig. 12.1). Dry nitrogen was passed over the powder to remove the last traces of alcohol.

Since 1948 all beryllium sources have been made by a volatilization method. The polonium is volatilized into one part of a metal container. Loose beryllium powder, or powder that has been cold-pressed to fit the container, is added. The container is then assembled and coated with about 0.020 in. of nickel which covers any contamination and seals the container. At this stage the sources are 20 to 40 per cent efficient. They are heated to about 600°C to distribute the polonium throughout the beryllium. The completed sources are usually 75 to 90 per cent efficient. Figure 12.2 presents a view through a water-barrier window in a shielded hood which shows the remote-operated volatilization equipment.

On some occasions polonium deposited on platinum has been inserted into the source container. The polonium on platinum has been covered with an alpha range of nickel to permit assembly without bodily exposure to neutrons. The sealing and distribution are carried out as described above. A slightly higher volatilizing temperature is required to get the polonium through the nickel layer, and the neutron efficiency may be a little less than when a nickel covering is not used.

1.8 *Polonium-Boron Neutron Sources.* Boron is a nonmetal and will not deposit polonium from a solution. The volatilization technique used for beryllium sources cannot be used because boron is a poor conductor. When polonium and boron are heated to 600°C in a sealed metal container, a high neutron efficiency is reached. Upon cooling, the polonium is redistributed to the more rapidly cooling metal and develops a neutron efficiency of 10 to 20 per cent.



NOTE: TYGON TUBING WAS USED THROUGHOUT

*ALL STOPCOCKS HAVE 120° BETWEEN OPENINGS

Fig. 12.1—Semiremote-controlled apparatus for making neutron sources.

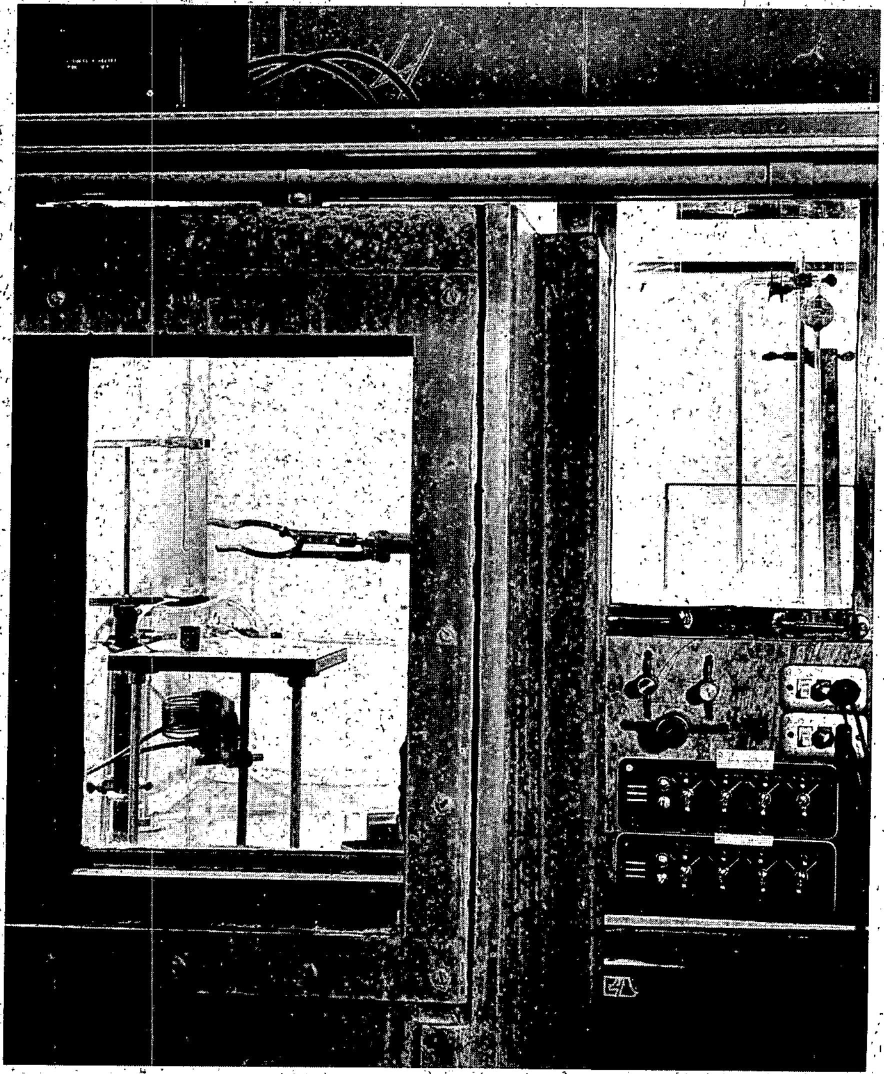


Fig. 12.2—Remote-operated volatilization equipment seen through a water-barrier window.

A method has been developed for preparing boron sources by volatilization. The boron powder at room temperature is vibrated while the polonium is slowly volatilized from a metal gun with a nozzle extending into the powder. This method is useful for sources incorporating up to

50 curies of polonium and has the advantage over evaporation methods of introducing pure polonium into the source.

The number of boron sources prepared is small; hence they are usually made by an evaporation method which can be set up simply at any time. Polonium is dissolved in hydrochloric acid, and this solution is evaporated from boron powder in a glass vessel. Neutron efficiencies of 80 to 90 per cent are attained when the depth of boron powder does not exceed 1 mm. The temperature of evaporation is kept below 150°C to prevent loss of volatile polonium chloride.

The evaporation method is useful for any size source. Sources up to 300 curies have been made by incremental evaporations and by combining the portions of boron. Several evaporations per source serve to give high neutron efficiency and reduce personnel exposure to neutrons.

1.9 *Polonium-mock-fission Neutron Sources.* Several salts have been used in attempts to produce neutron sources simulating the fission spectrum. The combination of salts now used is sodium fluoborate and sodium fluoberyllate with a mole ratio of B : Be = 24 : 1.

To prepare a source from any salt, the polonium is dissolved in an acid having the same radical as the salt, and the acid is removed by evaporation. Hydrofluoric acid is used in making mock-fission sources. Fluoborates are unstable at elevated temperatures, and the evaporation is done below 150°C. Since platinum must be used to withstand hydrofluoric acid, evaporations are made in thin platinum vessels which can be cut or pressed to the shape of the finished source. The platinum vessel is coated directly or placed in an outer container and coated with nickel.

1.10 *Miscellaneous Neutron Sources.* Lithium and sodium sources are made by placing polonium in a nickel container through volatilization, adding the alkali metal, sealing with nickel, and heating above the melting point of the alkali metal. Polonium-plated platinum vessels which conform to the shape of the nickel container are also used in making sources of this type.

Sources from polonium and magnesium or aluminum are made by the volatilization method used for beryllium sources.

Some liquid neutron sources have been made because the homogeneity of a solution offers the possibility of a reproducible neutron standard; however, solutions of radioactive materials are not stable. Sources prepared from antimony pentafluoride[10] and solutions of beryllium in hydrochloric acid were not stable enough for standard neutron sources. In addition, the path of an alpha in liquids is so short that only about 10 per cent efficiency is realized; hence calibrated solid sources are used exclusively for standards.

1.11 *Efficiency of Neutron Sources.* The theoretical neutron yields given in Table 12.1 are used to calculate efficiencies of sources. When pure polonium is used, the efficiencies of beryllium and boron sources are about 95 per cent if the ratio of polonium to target is small. Decrease in efficiency with an increase in the polonium-to-target ratio is known better for beryllium than for other target elements. As the ratio reaches 50 curies per gram of beryllium, the neutron efficiency decreases to about 75 per cent. What data are available for boron sources indicate a similar trend.

The surface area of 230- to 325-mesh beryllium powder, as measured by Hertz,[11] is 2400 sq cm/g. For a monoatomic layer of polonium on 1 g of this powder, 3.4 curies of polonium are required. With 50 curies of polonium per gram of beryllium, there are 15 atomic layers. The thickness of polonium is not great enough to absorb appreciable alpha energy; however, neutron yield decreases rapidly as alpha energy decreases.

Efficiencies of 90 per cent can be attained for mock-fission and other salt sources. The specifications for such sources usually are for high ratios of polonium to target, and most sources are in the range of 60 to 70 per cent efficient.

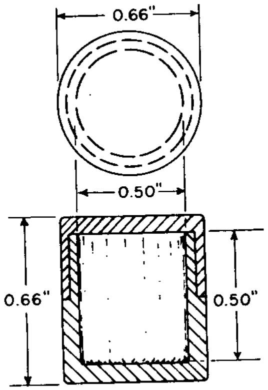
1.12 *Containers for Neutron Sources.* Aluminum and brass were used for some of the early source containers; however, nickel is now used for most source containers, except for special containers requiring steel, platinum, or beryllium.

Some sizes and shapes of source containers are shown in Fig. 12.3. The standard container is a nickel right cylinder 0.66 in. O.D. by 0.66 in. high with 0.08-in. walls, before sealing. When finished, the dimensions are 0.70 in. O.D. by 0.70 in. high. Containers as small as 0.20 in. in diameter are sometimes made. If the amount of polonium in a source is to be determined by a sensitive calorimeter, dimensions must not exceed $1\frac{1}{8}$ in. in diameter by 3 in. in length.

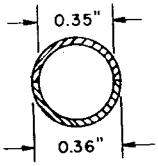
1.13 *Sealing Source Containers.* The first neutron sources made at the Dayton Project were solder-sealed. Dipping in solder covered up contamination on the outer surface. Frequently, decontamination was not complete, and a coating of paint or plastic was applied.

All sources are now sealed with nickel obtained from the decomposition of nickel carbonyl. The containers are automatically decontaminated by the nickel coating which should have a thickness of about 0.02 in.

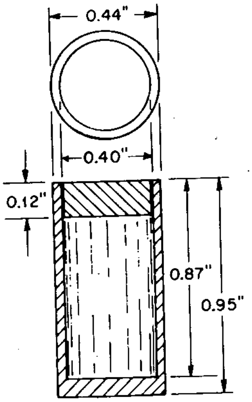
Neutron sources to be used at high temperatures are sealed with nickel and placed in a second container which is closed by welding. Polonium-beryllium neutron sources have been held at 850°C for 6 months with only a small decrease in neutron efficiency. Source efficiencies



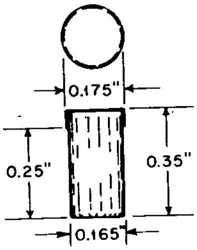
(a)
STANDARD NICKEL CONTAINER
HEIGHT OR DIAMETER MAY
BE VARIED IN SPECIAL CASES.
DIMENSIONS ~ 0.70" x 0.70"
WHEN NICKEL COATED



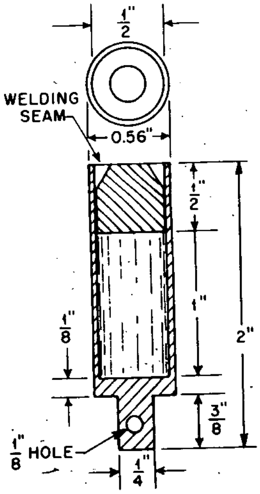
(b)
NICKEL OR
PLATINUM SPHERE.
DIMENSION 0.40"
WHEN COATED



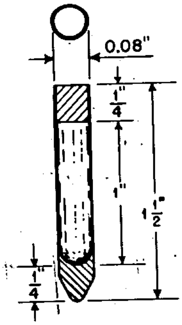
(c)
NICKEL CONTAINER
TO BE COATED
AND INSERTED IN
WELDED CONTAINER
SHOWN IN (d)



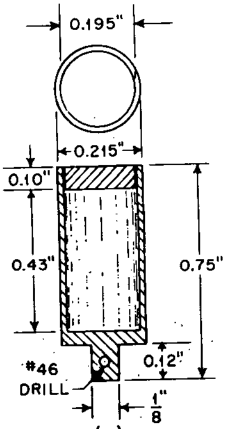
(e)
PLATINUM CAN OF
5-MIL WALL. DIMENSIONS 0.22" x 0.40"
WHEN NICKEL
COATED



(d)
#347 STAINLESS
STEEL FOR HIGH-TEMPERATURE SOURCES



(f)
NICKEL CONTAINER
WITH 5-MIL WALL.
DIAMETER 0.10"
AFTER NICKEL
COATING



(g)
NICKEL CONTAINER
WITH EYELET

Fig. 12.3—Neutron-source containers.

are held better at high temperature when iron or beryllium is used for the source container.

Most sources are sealed at a pressure not exceeding 5 cm Hg. Boron sources of high curie value are sealed at a pressure of about ½ atm. The higher pressure is used to lessen migration of polonium chloride.

1.14 *Equipment for Source Preparation.* A well-ventilated hood (Fig. 12.2) is necessary for handling any radioactive material. For preparing neutron sources, a hood should have utilities accessible from the outside to prevent exposure of personnel. Shields are provided at Mound Laboratory to reduce irradiation of workers.

Polonium is transferred to source containers by heating it to a red heat *in vacuo.* Induction heating effects polonium transfer in a few minutes. An apparatus is also in use in which polonium is transferred by use of resistance heaters. The course of a polonium transfer is followed by counting the 0.8-Mev gamma of polonium with a lead-shielded G-M tube. To take gamma counts, transfer of polonium is made before addition of target to the source container since many alpha-neutron reactions are accompanied by gamma emission.

The resistance-heated apparatus, together with a gamma counter, is used for transferring increments of polonium.[12] The polonium is placed at the bottom end of a metal gun about 5 in. long. Heat is applied at the top of the gun at such rate that the transfer of polonium can be extended over several hours. A slow rate of transfer permits high accuracy of increment volatilization.

The assembling of sources is done with tongs 1 or 2 ft in length, behind shields (Fig. 12.2), or with remote-controlled apparatus.[13]

Nickel coating of sources is done in a vacuum system as free as possible from leaks. Oxygen interferes with the coating process. Even minute concentrations of oxygen cause the nickel to be brittle. Small induction heaters of 50 watts output are used to closely control the temperature of sources and the rate of decomposition of nickel carbonyl.

The neutron emission of a source in preparation is followed by a neutron probe (see Chap. 9) consisting of a boron-lined tube, paraffin moderator, and counting circuit similar to that shown in Fig. 12.4.

When the reduction and deposition method was in use for preparing beryllium sources, it was desirable to follow the polonium concentration of the solution. For that purpose an immersion alpha counter was developed by Birden.[14,15] A quartz tube with an alpha-transparent window was immersed into the solution. The end of the quartz tube containing the window was attached to a proportional counting tube. The other end of the quartz tube which dipped into the solution permitted the polonium to come into contact with the window for alpha counting. The immersion counter (Figs. 12.5 and 12.6) was useful in the range of

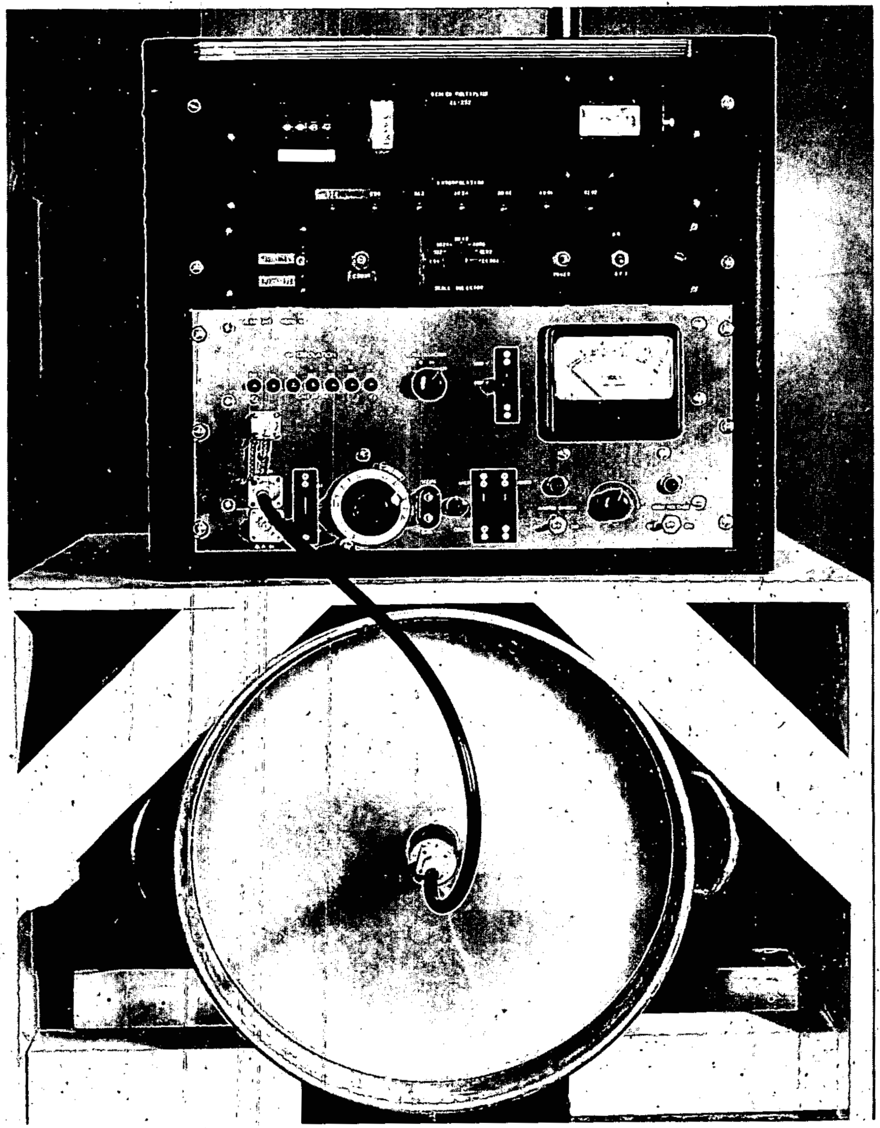


Fig. 12.4—Neutron-counting equipment.

0.1 mc to 3 curies per milliliter of solution and was so made that the range could be extended.

The amount of polonium in a neutron source is determined to about 0.1 per cent in a calorimeter. Gamma and neutron radiation absorbed in the calorimeter is negligible in comparison to alpha radiation (Chap. 10).

A neutron counter is essential in the preparation of neutron sources. Unknown sources are compared with standards by use of a boron-lined tube in a Hanson-type[16] paraffin moderator.

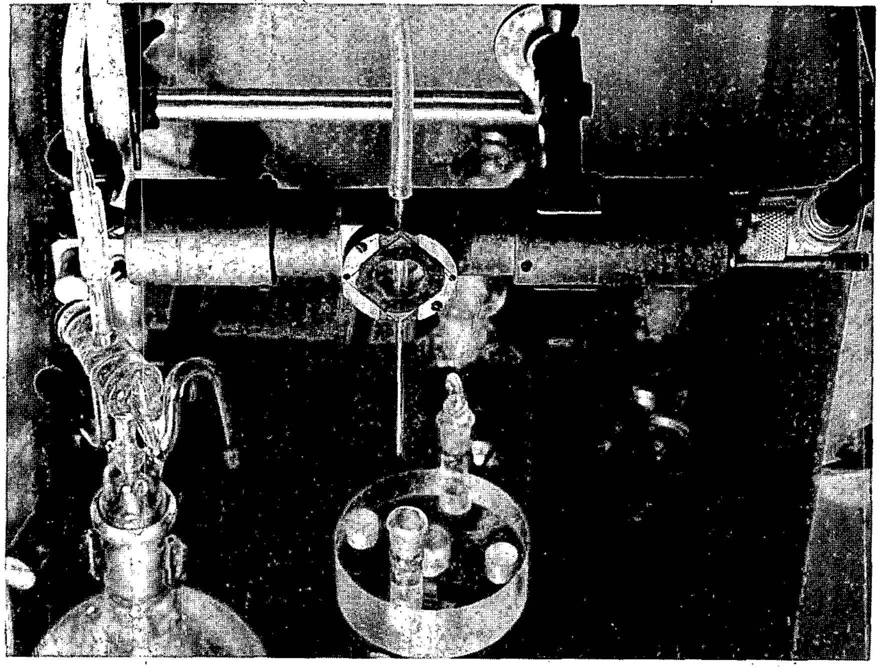


Fig. 12.5—Immersion alpha counter.

1.15 *Neutron Counting.* The neutron has no charge and is counted indirectly. The principal reactions used are neutron-alpha, neutron-proton, and neutron capture producing a beta emitter. The last reaction is used to determine absolute neutron emission, and the first two reactions are used to compare unknowns with standards.

The Szilard-Chalmers method[1] uses beta-emitting manganese as one means of counting neutrons. Exposure of the permanganate solution to neutrons, precipitation and recovery of manganese dioxide, and beta counting is laborious and time-consuming.

Probably the most accurate method of calibrating a neutron standard uses indium foils which are inserted into a graphite block. The foils

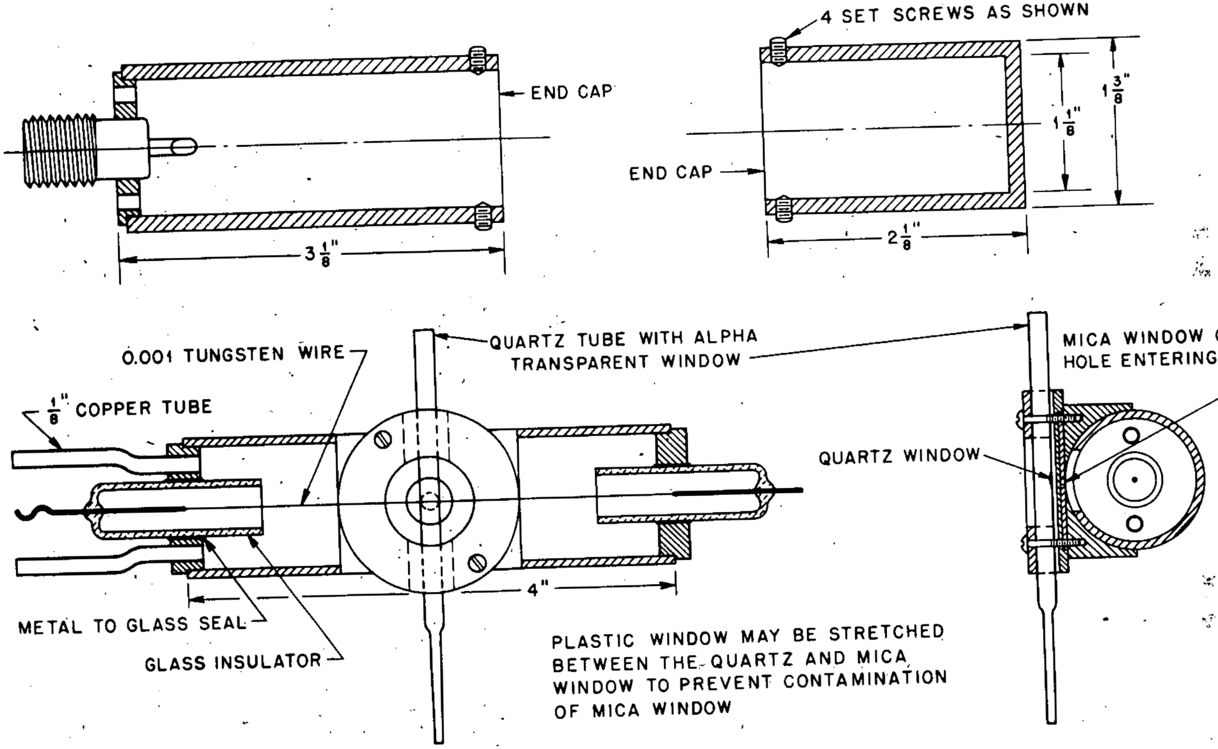


Fig. 12.6—Construction of immersion alpha counter.

are placed in the block at various distances from the neutron source (which is mounted in the same block), and the neutron emission is determined by integration of the beta counts from the irradiated foils. Neutron counting with indium foils has not been practiced at Mound Laboratory; however, calibration of primary neutron standards for Mound Laboratory used the indium-foil technique.

When a primary standard is available, unknowns are quickly and accurately compared with it by use of a boron-lined or BF_3 tube in a paraffin moderator of the Hanson type.[16] In using the Hanson-type counter, sources of varying neutron energies must be placed a sufficient distance from the counter to give a linear response. Neutron standards used at Mound Laboratory prior to 1949 agreed well with the standards established at that time. However, comparison counting was not so accurately done prior to 1949 because small sources were placed too close to the counter to obtain linear response.

Radium-beryllium, polonium-beryllium, and polonium-mock-fission standards were calibrated in 1949. New polonium-beryllium and polonium-mock-fission standards are prepared as needed and calibrated against their previous standards and the radium-beryllium standard. The radium-beryllium standard is corrected according to the equation

$$\text{Neutron change} = 1 + 0.100\ (1 - e^{-t/22})$$

where t is the time in years. The neutron change is due to the length of time required for radium-D to equilibrate with its predecessors.

It has been shown that the several kinds of neutron sources can be accurately compared when placed at least 50 cm from a Hanson-type counter.[17] Accurate comparisons are made at closer distances if calibration curves are used.

1.16 *Temperature of Neutron Sources.* The temperature of a neutron source depends upon its physical size and curie content. The heat liberation of 1 curie of polonium is 27.54 calories/hr or 0.032 watt (Chap. 10). Standard beryllium sources of 4.2 and 22.6 curies reached temperatures of 30 and 56°C in air, respectively.[6] The temperature reached *in vacuo* is much higher, and care must be taken to keep boron and mock-fission sources from exceeding a temperature of 150°C. Beryllium sources are usable at temperatures as high as 850°C if they are especially prepared.

1.17 *Radiation from Neutron Sources.* Neutrons and gammas are the only radiations emitted from neutron-source containers. The gammas consist of those from polonium and those from alpha-neutron reactions. Polonium emits about 1.7×10^{-5} gamma of 0.8 Mev energy per alpha. A polonium-beryllium neutron source emits about 0.7 gamma of

4.4 Mev energy per neutron. The energies of gammas from polonium neutron sources have been determined by Hertz and Breen[18] with a crystal spectrometer and are given in Table 12.2.

Average energies of neutrons from polonium-beryllium, polonium-boron, and polonium-mock-fission sources are reported in the literature as 4.5, 2.3, and 2.0 Mev, respectively. A program is under way at Mound Laboratory to determine neutron energies.

Table 12.2—Gammas from Polonium Neutron Sources

Element	Reaction	Energy of gammas, Mev
Lithium	$Li^7(\alpha,\alpha')Li^7$	0.483
Beryllium	$Be^9(\alpha,n)C^{12}$	4.45
Boron	$B^{11}(\alpha,n)N^{14}$	2.36
	$B^{10}(\alpha,p)C^{13}$	3.68
Fluorine	$F^{19}(\alpha,n)Na^{22}$	1.28, 1.51
	$Na^{22} \rightarrow Ne^{22} + \beta^+$	1.28
Sodium	$Na^{23}(\alpha,p)Mg^{26}$	0.43, 1.13, 1.83, 2.57
Magnesium	$Mg^{25}(\alpha,n)Si^{28}$	4.0
	$Mg^{24}(\alpha,p)Al^{27}$ $Mg^{25}(\alpha,p)Al^{28}$	1.01
	$Al^{28} \rightarrow Si^{28} + \beta^-$	1.82
	$Al^{29} \rightarrow Si^{29} + \beta^-$	1.30, 2.32
Aluminum	$Al^{27}(\alpha,p)Si^{30}$	1.25, 2.28, 3.55

1.18 *Radiation Tolerances.* At present the limit for total body radiation is 0.3 r/week, 60 mr/day, or 7.5 mr/hr. One milliroentgen per hour of radiation is given approximately by: 10 fast neutrons/sec/sq cm, 234 slow neutrons/sec/sq cm, and 530 1-Mev gammas/sec/sq cm.

Shipping regulations of the Interstate Commerce Commission permit 200 mr/hr total radiation at the surface of a container or 10 mr/hr at 1 meter from the source of radiation.

1.19 *Shielding Neutrons.* As explained earlier in this chapter, neutrons are thermalized by fewer collisions with light elements than with heavy elements. However, because the heavier elements have higher densities, the thicknesses of various materials required to thermalize fast neutrons are not greatly different. The thickness of a substance which will thermalize one-half the neutrons incident on it is called its "half-thickness." When the half-thickness is known, the number of fast neutrons penetrating a shield of thickness R is given by

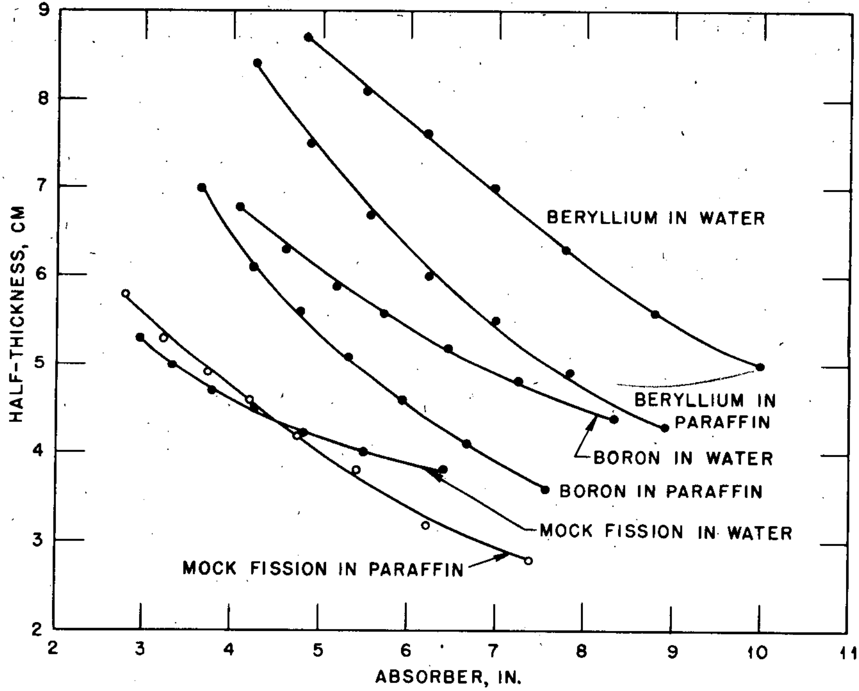


Fig. 12.7—Effect of absorber thickness on half-thickness.

$$n = \frac{N}{4\pi R^2} \times \frac{1}{2^{R/t}}$$

where n = fast neutrons through the shield
N = strength of neutron source, neutrons per second
R = thickness of shield, centimeters
t = half-thickness of shield, centimeters

Half-thicknesses have been determined with good precision for water and paraffin, and, roughly, for several metals.[6] Half-thicknesses of most materials are 5 to 6 cm. The variations in half-thicknesses of paraffin and water are shown for several types of neutron sources in Fig. 12.7.

Steel drums filled with paraffin are used to transport neutron sources under Interstate Commerce Commission regulations. Water-filled drums are sometimes used when sources are transported by Atomic Energy Commission carrier.

1.20 *Uses of Neutron Sources.* Neutron sources are used in starting uranium reactors, calibrating instruments, simulating fission spectra, making biological radiation shielding experiments, and in oil-well logging.

1.21 *Number and Size of Neutron Sources.* Hundreds of neutron sources have been made at this laboratory since the first one was made in 1945. Polonium has been used in increasing amounts as the demand for neutron sources has increased. The average-size neutron source fabricated at Mound Laboratory contains approximately 5 curies of polonium.

Both polonium-beryllium and polonium-boron sources have been made with neutron emissions in excess of 10^8 neutrons/sec.

Several series of polonium-beryllium sources were made in which the spread in neutron emission between individual sources was not over 5 per cent. In one group of eight sources, four sources had neutron emissions consistent to within 1 per cent of each other. Another group of eight sources was made to produce four pairs of sources with a spread in neutron emission of 0.2 per cent between each pair.

2. ALPHA SOURCES

2.1 *Introduction.* The alpha radiation from Po^{210} is essentially monoenergetic at 5.298 Mev (Chap. 2). The small amount of polonium per curie means that alpha sources with negligible self-absorption can be made. Polonium migrates readily and gives serious contamination problems. For this reason, uncovered alpha sources are supplied only to those experienced in the handling of polonium.

The needs of people doing research with alpha radiation are so varied that little attempt is made to make a standard alpha source; rather, each source is made to fit the needs of a particular experiment.

2.2 *Alpha-source Coverings.* The range of a polonium alpha is only 3.84 cm in air and less than 0.0025 cm in metals. To make covered alpha sources which are rugged and absorb little alpha energy requires strong thin films.

The thickness of a material which will absorb the energy of an alpha is given approximately by: milligram per square centimeter (equal to 1 cm of air) = 0.3 $\sqrt{\text{atomic weight}}$, which, for polonium, becomes 3.84 × 0.3 $\sqrt{\text{atomic weight}}$ for the full range of the alpha. The thickness of the absorber in centimeters is then

$$\frac{1000 \text{ mg/sq cm}}{\text{Density}}$$

The thicknesses of selected substances which will absorb the energy of polonium alphas are given in Table 12.3.

Mica can be split to a thickness of 1 mg/sq cm or less, thus leaving alphas at least 80 per cent of their original energy. Mica windows are held to source holders with Apiezon wax and provide sturdy sources.

Aluminum is obtainable as thin as 0.00025 cm; however, it is not free from holes. Alpha radiation provides an oxidizing atmosphere in air which thin aluminum cannot withstand.

Table 12.3—Ranges of Polonium Alphas

Substance	Density, g/cu cm	Absorber thickness, mg/sq cm	Range of polonium alpha Cm	Range of polonium alpha In.
Mica	2.76 to 3.00	5.0	0.0018 to 0.0017	0.00071 to 0.00066
Aluminum	2.70	5.97	0.0022	0.00087
Titanium	4.5	7.97	0.0018	0.00070
Iron	7.86	8.60	0.0011	0.00043
Nickel	8.90	8.82	0.00099	0.00039
Tantalum	16.6	15.5	0.00093	0.00037
Gold	19.3	16.2	0.00084	0.00033
Platinum	21.45	16.1	0.00075	0.00030

Iron and nickel are too easily corroded in the presence of alpha radiation to be useful by themselves. Some stainless steels are corrosion resistant to alpha radiation and probably can be obtained in thicknesses which will emit alphas with 60 per cent of their initial energy.

Tantalum is available 0.000625 cm thick and can be polished somewhat thinner. When 0.000625-cm tantalum is used as a source cover, the alphas retain only 32 per cent of their initial energy. Such sources are sealed and, with care, can be used *in vacuo*.

Gold leaf 0.000004 in. in thickness is available. The leaf is porous and is used in multiple layers. Eight layers of this gold leaf leave alphas with 90 per cent of their original energy. Such sources are known to hold several weeks without leaking polonium.

Titanium and platinum of alpha-window thickness are not available; however, both metals are resistant to corrosion, and they should permit sources of high alpha energy to be fabricated.

2.3 *Preparation of Alpha Sources.* If polonium is in direct contact with a material, it is apt to diffuse through the thickness of an alpha window. To prevent diffusion through the window, polonium is placed in a 0.02- to 0.03-in. depression and the window is sealed to a surrounding rim.

Polonium is deposited on a noncorrosive metal, such as platinum, and is inserted in suitable plastic or metal holders. The polonium is volatilized onto the metal or is plated if uniform distribution is desired. Sometimes an acid solution of polonium is evaporated on the source holder. Polonium is also supplied as a nitrate in glass tubes.

Mound Laboratory fabricates about 25 alpha sources per year and these sources contain an average of about 150 mc of polonium each.

2.4 *Measurements on Alpha Sources.* The amount of polonium on an alpha source is usually too small to be calorimetered. An alpha counter of appropriate range is used to count the activity directly, or the amount of polonium electrochemically deposited from a solution is determined from the difference in alpha count of the solution before and after deposition.

Radioautographs give a rough measure of the distribution of polonium.

Alpha energies are calculated from absorber thicknesses.

2.5 *Transportation of Alpha Sources.* The source is placed in a glass or plastic holder, which is packed in a metal tube, and the metal tube is packed in a wooden box. Gamma rays are the only penetrating radiation from alpha sources. The amount of polonium in an alpha source seldom exceeds 1 curie; therefore there is no shielding problem.

REFERENCES

1. Samuel Glasstone, "Sourcebook on Atomic Energy," D. Van Nostrand Company, Inc., New York, 1950.
2. G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley & Sons, Inc., New York, 1949.
3. James M. Cork, "Radioactivity and Nuclear Physics," D. Van Nostrand Company, Inc., New York, 1947.
4. Herbert L. Anderson, Neutrons from Alpha Emitters, Report NP-851, December 1948.
5. F. J. Leitz, Jr., Specifications for the Mock-fission Neutron Source Requested by the Metallurgical Laboratory, Report MLM-46-2-53, Feb. 26, 1946.
6. J. L. Richmond, Neutron Sources from Polonium, Report MLM-641, Dec. 5, 1951.
7. W. J. Argersinger, Jr., J. H. Birden, G. O. Gutekunst, Jr., F. J. Leitz, Jr., and R. M. Watrous, The Preparation of Neutron Sources, Report MLM-M-588, June 30, 1946.
8. J. H. Birden, A Report of the Work Done in Preparing Neutron Sources from Polonium and Beryllium Between Aug. 5, 1945, and May 25, 1947, Report MLM-187, Sept. 13, 1948.
9. J. H. Birden, Preparation of Polonium-Beryllium Neutron Sources by Spontaneous Deposition, Report MLM-297, Mar. 21, 1949.

10. L. L. Bentz, A Report on Lithium, Sodium, and Liquid-Neutron Sources, Report MLM-312, Apr. 22, 1949.
11. J. L. Richmond and M. R. Hertz, Progress Report, Report MLM-139, June 1–30, 1948, p. 4.
12. J. H. Birden, Progress Report, Report MLM-602, Apr. 2 to July 2, 1951, p. 46.
13. M. R. Hertz, Progress Report, Report MLM-602, Apr. 2 to July 2, 1951, p. 50.
14. J. H. Birden and J. L. Richmond, Progress Report, Report MLM-443-4, January, February, and March 1950, p. 4.
15. J. L. Richmond, Progress Report, Report MLM-683, Mar. 31, 1952, p. 13.
16. A. O. Hanson, Flat Response Neutron Detector, Report LAMS-66, Mar. 15, 1944.
17. M. R. Hertz, Progress Report, Report MLM-379-2, July, August, and September 1949, p. 235.
18. M. R. Hertz and R. J. Breen, Gamma Radiation from Neutron Sources, Report MLM-871, July 17, 1953.

Chapter 13

HEALTH PHYSICS

By Warren L. Hood and John S. Stanton

1. INTRODUCTION

Health Physics is primarily concerned with the protection of personnel from the radiological hazards accompanying the formation, concentration, handling, storing, and use of radioactive materials. The science of Health Physics originated about the time that the Manhattan Engineer District (which was the predecessor to the Atomic Energy Commission) was established. Subsequent to its inception, the Dayton Project instituted a Health Physics program for the protection of personnel from the hazards associated with the handling of radioactive materials.

The responsibilities of the health physicist at the Dayton Project and Mound Laboratory include:

1. The establishment of standards of safe levels of exposure to all types of radioactive emissions.
2. The detection of these radiations under a wide variety of conditions.
3. The interpretation of the data collected on routine and special laboratory area surveys.
4. The development of suitable methods of personnel protection from radiation hazards.
5. The indoctrination of personnel in health physics procedures.

The Health Physics procedures in this chapter are applicable to all radioactive elements which have been handled at the Dayton Project and at Mound Laboratory.

2. ESTABLISHMENT OF LIMITS OF PERMISSIBLE EXPOSURE

2.1 *General.* During the formative years of the atomic energy program, little was known of the permissible limits of exposure of personnel to the alpha, beta, gamma, and X radiation from the naturally occurring radioisotopes. The Advisory Committee on X-ray and Radium

Protection of the National Bureau of Standards had prepared a publication (Handbook No. 20) setting forth the then acceptable personnel exposure limits to X rays and radium, and this publication was one of the earliest reference sources used for the establishment of maximum permissible radiation exposure levels. The data on permissible exposure levels at the disposal of the health physicist became obsolete as soon as large concentrations of purified natural and artificially produced radioisotopes were made available, and information was accumulated on the characteristic radiations of these radioisotopes. Advances in the field of health physics, which are based on the acquisition of new and recent data, are incorporated into revisions of permissible exposure limits. It is the usual procedure for the health physicist to direct attention to each radioisotope and its characteristic radiation on an individual basis, when this is possible, and to establish personnel exposure limits which are based on recently acquired data on the isotope.

2.2 *Permissible Polonium Exposure Levels at the Dayton Project and Mound Laboratory.* Early in 1944 W. F. Bale[1] recommended that not more than 1 μc of polonium should be ingested. This figure was later revised to a maximum total polonium content in the body of 2.25 μc and was based on an assumed urine excretion rate of 0.1 per cent per day of the polonium in the body. Further modifications of the acceptable exposure levels were suggested from time to time, until K. Z. Morgan[2] recommended a value which is the accepted standard at Mound Laboratory at this time. Morgan's recommendation was based on the work of R. M. Fink[3] at the University of Rochester.

The maximum permissible value for airborne polonium was originally established at 2400 dis/min/cu meter. This value was derived from various assumptions as to the amount of air inhaled during a working day, the per cent of inhaled polonium that is absorbed by the body, the per cent of the total polonium intake attributable to inhalation, the rate at which polonium is lost from the body by combined decay and excretion, and the belief that the lungs did not concentrate polonium to any extent. A revised set of permissible airborne polonium levels was put into effect at Mound Laboratory in February 1949.

Values for the permissible levels of beta and gamma radiation and for permissible surface contamination within, and adjacent to, the working area used for the purification of polonium have been in effect since the inception of the Dayton Project. The acquisition of more knowledge on the effects of these radiations has resulted in reappraisals of the acceptable permissible levels.

Comparative values of the former and present permissible levels for polonium and for beta- and gamma-emitting radioisotopes are tabulated in Table 13.1.

The radioactive impurities which are present in the polonium purification process (Chaps. 6 and 7) and the handling of other types of radioactive isotopes necessitated the establishment of the maximum permissible levels of exposure to beta and gamma radiation which are tabulated in Table 13.1.

Table 13.1—Permissible Levels for Polonium and for Beta- and Gamma-emitting Radioisotopes

Sample	Former (prior to Apr. 1, 1951)	Present
Beta or gamma	0.5 r/week	0.3 r/week
Urine	3000 dis/min/24-hr sample	500 dis/min/24-hr sample
Air level	2400 dis/min/cu meter	1000 dis/min/cu meter
Wipe:†		
White	1500 dis/min/wipe	500 dis/min/wipe
Yellow	1500–10,000 dis/min/wipe	500–2000 dis/min/wipe
Red	10,000 dis/min/wipe	2000 dis/min/wipe

†At one time the working areas at the [redacted] were classified according to the amount of contaminati[redacted]. For convenience the areas were color coded as presente[redacted] table.

3. HEALTH PHYSICS INFLUENCE ON LABORATORY DESIGN

3.1 *Confinement of Radioactivity.* During the early years of the Dayton Project the number of personnel with greater than permissible values of polonium in their urine prompted the development of completely enclosed compartments for the handling of polonium.[4] The design of these compartments was based on three major premises:

1. The presentation of an impenetrable barrier between the operator and the compartments containing radioactivity.
2. The maintenance of a pressure differential between the operating area and those compartments so that any leakage of radioactivity through the barrier would be from regions of lower to higher radioactivity levels.
3. The elimination of as many horizontal surfaces on the operator's side of the compartment as possible to prevent the accumulation of radioactive dust.

Design specifications for these compartmentalized processing hoods required that all operations inside the hoods be performed through sealed glove ports or by the use of extensions to enclosed valves, etc. Utility services and the introduction of reagents into the hoods are controlled from the front of the hood. The processing of polonium is accomplished in a series of hoods similar to those shown in Fig. 13.1.

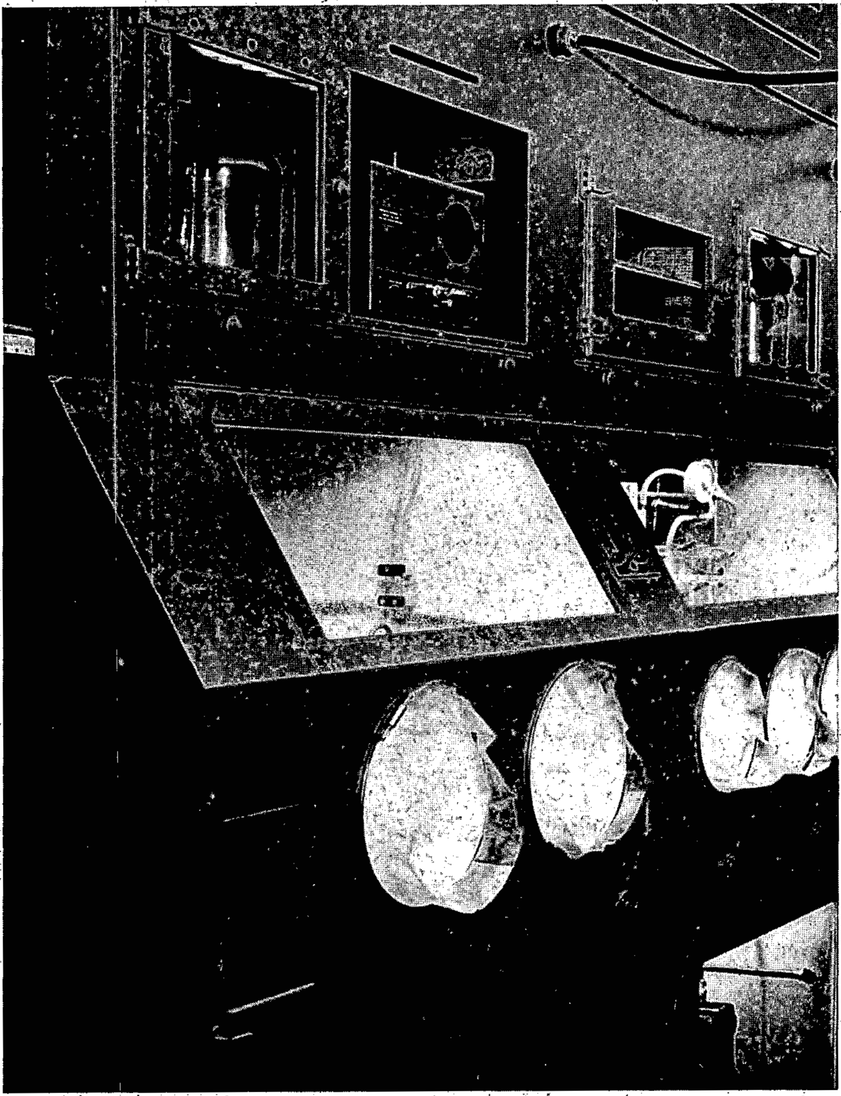


Fig. 13.1 — Typical polonium-processing hoods.

3.2 *Ventilation Systems: Pressure Differentials.* The spread of radioactive contamination is minimized by maintaining air pressure differentials between areas having different concentrations of radioactivity. Four such pressure-regulating systems are in use at Mound Laboratory. The air pressure in each system is adjusted so that, if leaks occur, air flows from the main laboratory corridors into the individual laboratories, then from these into the service corridor (area behind the hoods), and finally into the hoods. Each hood is equipped with an air filter, and the outlets of all these filters are discharged into a common filter bank which discharges through an exhaust stack into the atmosphere.

Area air pressures and air change rates in effect at Mound Laboratory at this time are given in Table 13.2.

Table 13.2 — Pressure Differentials and Air Change Rates at Mound Laboratory

Area	Pressure, in. above atmospheric	Air change rate
Main corridor	0.20	10–12 per hr
Individual laboratory	0.15	10–12 per hr
Service corridor	0.10	16 per hr
Hood	0–0.05	1 per min

3.3 *Interarea Traffic Procedures.* Where the confinement of radioactivity is of extreme importance, the design of a laboratory must allow for essential traffic between areas handling different quantities of radioactivity. In some areas it is advisable to require a complete change of clothing before entry is gained; hence facilities are provided for the storing of personal clothing and for the supply of apparel to be worn in the higher risk area. Air locks, locker rooms, shower stalls, and laundry facilities are also effective in controlling the spread of radioactivity. Interarea traffic at Mound Laboratory is routed through sections of the laboratory that incorporate these facilities.

3.4 *General Laboratory Design.* The use of compartmentalized polonium-processing hoods has proved to be a major advance in preventing the spread of radioactivity at Mound Laboratory. On those occasions when unavoidable accidents occur and polonium is introduced into working areas, effective decomtamination must be attained. Some of the factors which assure ease in decontaminating are the use of smooth, hard, nonporous surfacing for floors and walls, laboratory design which minimizes the number of horizontal surfaces, the use of enclosed storage spaces, and the use of materials of construction which are unaffected by strong decontamination agents.

4. CONTROL OF RADIOACTIVE CONTAMINATION

4.1 *Area Classification.* Laboratory areas are classified according to the nature of the work done within the area and the quantities of radioactivity normally treated in the area. Area classification procedures have been established at Mound Laboratory which govern

1. Travel between areas.
2. The wearing of protective clothing.
3. The use of personnel monitoring devices.
4. Methods of decontamination.
5. Methods of area monitoring.
6. Transfer of equipment between areas.
7. The establishment of safe working conditions.

Areas may be classified as "cold," "low risk," "high risk," and "hot." Cold areas are those in which no radioactive material is handled and the contamination level is essentially zero.

Low-risk areas are those in which all radioactive materials are confined in sealed storage spaces, hoods, or other suitable containers. The contamination level in an area of this classification is generally quite low.

The areas behind the hoods (service corridors) and other regions where there is a high probability of exposure to hazardous amounts of radioactivity are classified as high-risk areas.

The inside of hoods and the intake of filter banks are classified as hot areas since they generally have high levels of radioactive contamination present.

4.2 *Operating Procedure in Event of a Spill of Radioactive Material.* The accidental release of appreciable amounts of polonium, which is often referred to as a "spill," into a working area demands immediate action on the part of both the personnel involved in the accident and the health physicist. Those personnel in the laboratory where the spill occurred immediately hold their breath, assure themselves that further spills are not likely to occur, and vacate the room. Others are prevented from entering the contaminated laboratory until after a health physicist has been notified of the accident and has arrived on the scene and been apprised of the pertinent details.

The health physicist takes charge and carries out the following procedures, though not necessarily in the order delineated:

1. Area is checked for evacuation of personnel.
2. The personnel from the contaminated area are checked for medical assistance and/or decontamination requirements.
3. The affected area is surveyed and an air sample is taken to determine the amount and extent of the contamination. Appropriate protective clothing and air masks are worn by the survey personnel.
4. The spilled material, if liquid in form, is absorbed with paper toweling to prevent a further spread of contamination.
5. The area is roped off and surveyed for contamination spread by the shoes of personnel involved in the accident.

6. The immediate area involved is decontaminated. Coverings are placed over instruments, desks, etc., to minimize the effects of fall-out of radioactive dust. Grossly contaminated objects are sealed in suitable paper (Sisalkraft or wrapping paper) containers for later decontamination. Laboratory notebooks are sealed in large manila envelopes.

7. The general area in proximity to the laboratory involved in the spill is decontaminated by soap and water, bleach, or other decontaminant scrubbing.

8. Surface-wipe and air-level samples are taken to determine whether or not additional decontamination is required.

9. General area surveys of adjacent laboratories and corridors are made.

10. If all surveys and air samples taken show results that are within permissible limits, the floor in the laboratory is waxed, and the laboratory is returned to the assigned personnel for occupancy.

4.3 *Removal of Radioactive Contamination.* Generally, different types of radioactive contaminants do not respond equally well to a given method of removal; hence effective decontaminants must be selected on the basis of past experience or a knowledge of chemical displacement between the contaminant and the solvent. The type of surface over which the contamination is spread will also affect the selection of a decontaminating agent.

Effective agents for the removal of polonium from various surfaces include sodium hypochlorite, soap powder or other detergent, abrasives, alcohol, acids, water, and strippable coatings of paint or plastic. The desired goal of decontamination procedures is the complete removal of all radioactivity; vigorous scrubbing using a cloth or stiff brush and one or more of the above cleansing agents has proved to be especially effective. Repeated scrubbings may be required to accomplish the desired degree of decontamination. Delicate instruments may be cleansed by wiping with a cloth that has been dipped in water and wrung nearly dry.

In those cases where complete decontamination cannot be attained by scrubbing, etc., the object in question is usually considered reusable when a wipe sample produces no counts.

5. MONITORING, SURVEYING, AND COUNTING RADIOACTIVITY

5.1 *Personnel Monitoring.* Early experiments[5] proved that appreciable amounts of ingested polonium are excreted as body waste products. The ease with which the analysis of urine for its polonium content can be performed has resulted in the standardization of this method as a routine means for personnel monitoring. The maximum excretion of polonium in urine occurs within 24 hr after ingestion, and routine urine collection schedules which take cognizance of this fact are in effect at Mound Laboratory. Urine samples may be collected at any time if exposure to polonium is suspected.

The processing of urine samples consists in acidifying the sample and plating (by chemical displacement) the polonium from this solution onto clean copper disks. The transfer of the polonium to the disk is increased by stirring the solution. This method of plating polonium on copper disks recovers an average of 86 ± 10 per cent of the polonium present.[6] The copper disks are then inserted into a parallel-plate ionization chamber, and their alpha activity is counted. Alpha counts greater than 12 per minute per 50 ml are sufficient cause to restrict the person whose urine produced this count value from working in a risk area.

Film badges and pocket chambers supplement the urinalysis program of personnel monitoring. All personnel assigned to risk areas at Mound Laboratory carry these supplementary monitoring devices during the performance of their duties.

The film badges consist of a packet of photographic film (Du Pont No. D552) mounted in a stainless-steel frame. Windows in the frame allow radiation to penetrate the film. The remainder of the frame is covered by a thin cadmium shield which is helpful in identifying the energy level of the radiation. The film in these devices is developed weekly and analyzed by a standard film densitometer. Calibration of the film is established through comparison with a series of films exposed to known radiation intensities and developed in the same solution and at the same time as those films worn by laboratory personnel.

The pocket chambers, which are shaped like fountain pens, are air capacitors which are charged to 150 volts before being used. Ionizing radiation penetrating these chambers tends to discharge the capacitors, and the residual charge at the end of a working day gives a measure of the amount of personnel exposure. The charge on the capacitor is measured daily by an electrometer circuit. Pocket chambers are usually carried in pairs so that if one is accidently discharged the second chamber will supply the exposure information.

5.2 *Air Monitoring.* Laboratory areas at Mound Laboratory in which polonium is handled or processed are continuously monitored, during the normal working day, for the airborne polonium content. Wall-mounted air samplers contain filter paper through which laboratory air is drawn at a rate of flow of 10 liters/min, which corresponds to the approximate average breathing rate of man. The air samplers are mounted about 5 ft above floor level, and this height agrees well with the nose height of the average man.

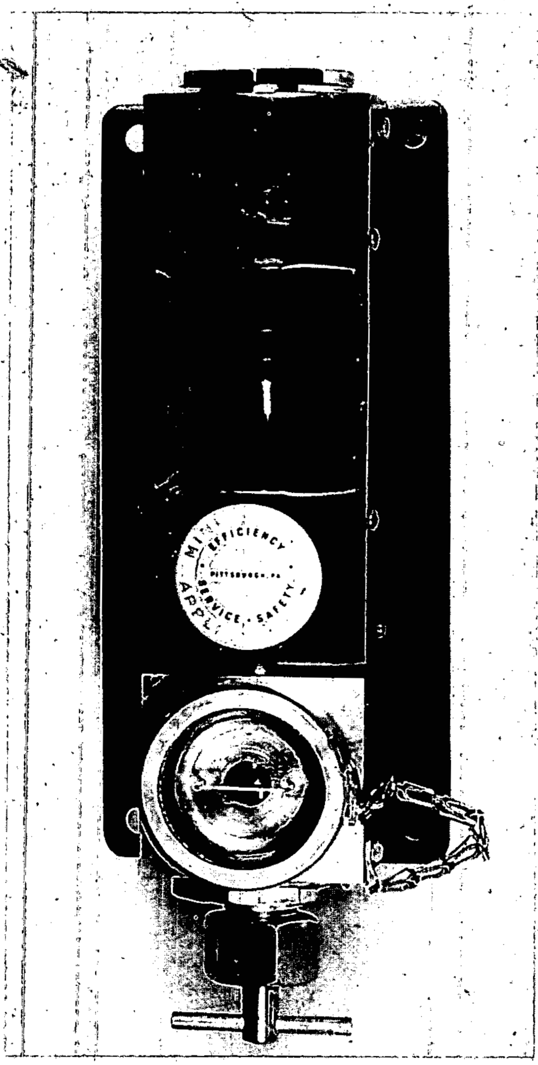


Fig. 13.2—Air sampler, wall type.

Two types of air samplers in use at Mound Laboratory are shown in Figs. 13.2 and 13.3. Air contamination levels in the main laboratory corridors and low-risk areas are monitored by the air sampler shown in Fig. 13.2, and high-risk areas are monitored by the air sampler shown in Fig. 13.3. The major difference between these two air samplers is in their method of construction. The high-risk-area air sampler is designed to fit through the wall of a laboratory in such a manner

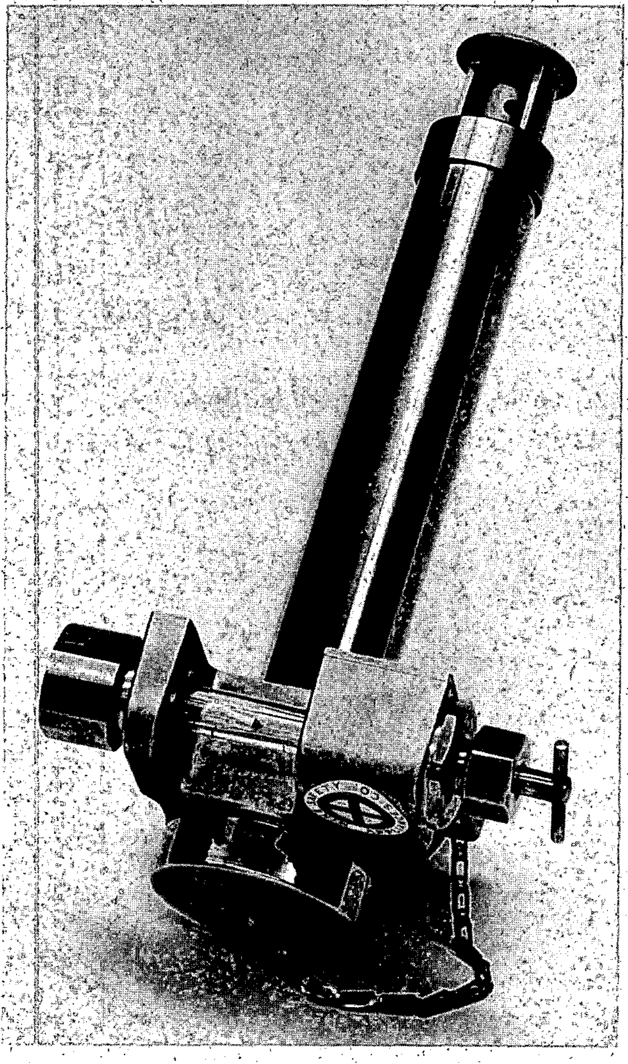


Fig. 13.3—Air sampler, remote type.

that the air from the high-risk area (back of the wall) is diverted through the filter paper which is accessible from a low-risk area. When the cap of this air sampler is removed to replace the filter paper, a spring-loaded gate closes the end of the air-sampler tube which extends into the high-risk area. This seals the low-risk-area room against entry of air from the high-risk area.

The normal flow of air in these air samplers is through the filter paper and into a vent which leads to the flow indicator (rotameter) and into the exhaust manifold of the vacuum pump. The vacuum pumps (The Spencer Turbine Co. type 7) will accommodate up to 80 air samplers and are capable of discharging 30 cu ft of air per minute against a 22-in. pressure head. The air from these pumps is discharged into the upstream side of the laboratory air-filter bank.

The downstream air from each filter is sampled for its polonium content before discharging into the exhaust stack. In most cases the sampled air from the downstream side of the filter bank is returned to the upstream side of the filter bank.

Filter papers from the air samplers are counted for their polonium content in parallel-plate alpha counters.

5.3 *Process Monitoring.* The processing of polonium and the fabrication of neutron and alpha sources involves radiation intensities that are potentially hazardous. These radiations, which include alpha, beta, gamma, and neutron emissions, are continuously monitored by a variety of instruments. Chapter 9 gives a description of some of these instruments.

Process monitors are usually equipped with audible or visual alarms which are actuated when maximum permissible exposure levels are exceeded. Occasionally it is desirable to make a permanent record of the amount of radiation emitted from a given process, and for these requirements the monitoring instrument is connected to a supplementary recorder.

5.4 *Laundry Monitoring.* Facilities for cleansing the clothing worn in risk areas at Mound Laboratory are provided by a laundry which is divided into two operating areas, a high-risk (hot) section and a low-risk (cold) section. Highly contaminated clothing is washed separately from slightly contaminated clothing to avoid gross contamination of all laundry operations and clothing.

Clothing is not released from the high-risk laundry until a health physics representative has monitored the clothing for its contamination level. No 100-sq cm section of clothing should indicate more than 5000 dis/min (20,000 dis/min for coveralls), as registered by a portable survey meter (Victoreen Model 356), before being released for reuse. If this contamination level cannot be realized after two washings in the high-risk laundry, the garment is discarded.

Slightly contaminated clothing is washed in the low-risk laundry. Contamination levels on the clothing from this section are monitored in the same manner as in the high-risk laundry. Towels, underclothing, and socks must register less than 2000 dis/min per 100 sq cm before they are released for reuse, whereas other clothing may indicate up to

5000 dis/min per 100 sq cm and still be usable. Polonium can be removed from white clothing through the use of citric acid, whereas in dyed clothing the polonium is tenaciously held and is very difficult to remove. Apparently, in the case of dyed clothing, polonium complexing occurs with agents introduced in the dyeing process.

Clothing worn in clean areas is spot checked for contamination. Personnel working in the risk sections of the laundry must wear protective clothing, which includes rubber boots and gloves, as well as submit to frequent surveys of the level of hand contamination.

5.5 *Surface Surveys.* Methods for locating radioactive contaminants on equipment, laboratory surfaces, and personnel include surface surveys by direct reading and surface surveys from wipe samples. The direct-reading survey is usually made with a portable, air-ionization, rate-meter instrument which is suspended directly above the surface being surveyed. Experience has indicated that, owing to the nature of polonium and its compounds, it is more important to evaluate contamination on loose dust rather than to take direct surface readings.

A technique for measuring removable surface contamination consists in wiping a 40-sq in. area with a 4.25-cm-diameter filter paper. A representative sample can be obtained by making six wipes with the filter paper across areas 1 in. wide by 6 to 8 in. long. These wipes are made at random within the area to be surveyed. A high degree of reproducibility is attainable with wipe surveys.

The wipe samples are evaluated by an air proportional alpha counter which is connected to a pulse-rate-meter circuit.

5.6 *Environmental Surveys.* Environmental surveys are those in which the area surrounding Mound Laboratory is monitored for its polonium concentration. Similar surveys were conducted around the facilities which constituted the Dayton Project. The manners by which polonium can escape into surrounding regions include the release of polonium through air exhaust systems, the transmittal from unknowingly contaminated clothing worn outside of the confines of the laboratories, and the transportation of polonium in the effluent waste from the laboratory areas. Sanitary sewers carried the effluent wastes from the Dayton Project because, at that time, no waste-disposal facilities were available and the sanitary sewers afforded a large dilution factor. Mound Laboratory has its own waste-disposal system which was described in Chap. 11.

Early environmental surveys at the Dayton Project consisted in taking air, water, mud, and vegetation samples at selected points surrounding the polonium production areas. With the city of Dayton as the center of the environmental survey area, sampling locations extended outward on each 15-deg radius for distances of 50 to 75 miles.

A second environmental survey route was shaped like a plus sign, and the intersection of the east-west and north-south routes occurred in proximity to Mound Laboratory.

The Great Miami River flows through the city of Dayton (where the Dayton Project was established) and adjacent to the city of Miamisburg, Ohio (where Mound Laboratory is located). Waste effluents are, and have been, discharged into this river, some before treatment for removal of the polonium and some after treatment. Surveys of the river near the points where the waste discharges into the river, and points further downstream, have been of particular interest in surveying for polonium. Figure 13.4 shows the mud and water survey routes along the Great Miami River, where sampling sites 8 and 9 are at the active-effluent-waste sewer outlet from the Dayton Project and sampling sites 42 and 43 are at the effluent-waste outlet from Mound Laboratory. Many of these sampling sites have been discontinued because it has been determined that very little polonium accumulated at these points. The frequency of sample collection at most of the remaining sampling sites has also been reduced.[7]

Similar type routes for environmental air surveys have been established, and Fig. 13.5 shows six of these routes on which air samples are taken at the numbered dots. The city of Miamisburg is at the center of the concentric circles at point No. 1.

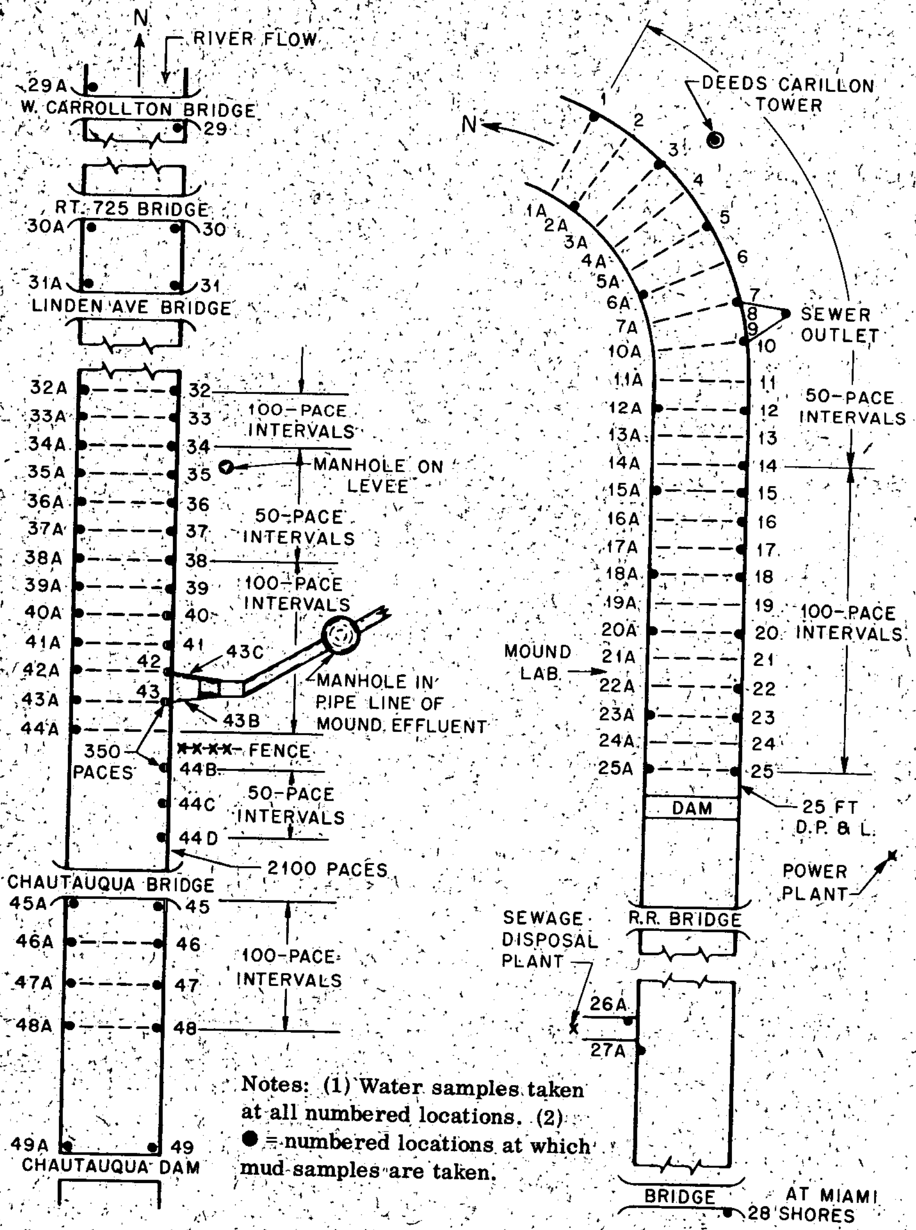
The processing of mud and water samples to recover the polonium for counting is accomplished through the use of simple operations.[8] The counting of the recovered polonium is done in parallel-plate alpha counters.

There have been no test results from any of the environmental sampling sites which showed excessive amounts of polonium present for any appreciable period of time.

5.7 *Health Physics Counting.* Samples collected by the Health Physics Section of Mound Laboratory are assayed for their polonium content by alpha counting of the sample. Types of samples evaluated in this manner include urine samples, air samples, wipe samples, and samples of mud, water, air, and vegetation obtained through environmental surveys.

Since the maximum permissible level of polonium is quite low, low-level alpha-counting techniques are employed. Counting rooms and alpha counters are kept scrupulously clean to maintain counting backgrounds as near zero as possible, and samples are counted for a sufficiently long time to attain acceptable statistical accuracy. Counting equipment must be stable in operation, free of spurious responses, and must be maintained in good operating condition.

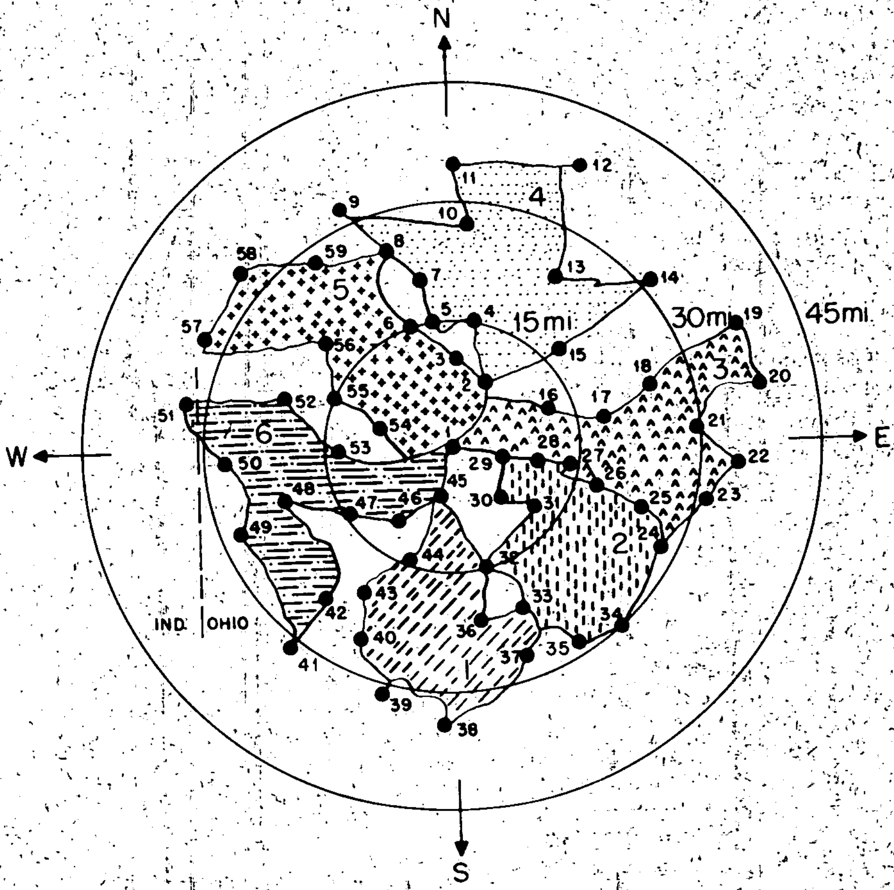
A separate counting laboratory is provided for low-level health physics counting. This laboratory is maintained in ultraclean condi-



Notes: (1) Water samples taken at all numbered locations. (2) ● = numbered locations at which mud samples are taken.

50. Franklin
51. Trenton
52A. New Miami
53A. 7 miles north of New Baltimore
54A. New Baltimore
55. Miamitown
56A. 5 miles north of Elizabethtown
57. Elizabethtown

Fig. 13.4—Great Miami River mud and water sampling routes.



1. Miamisburg
2. Dayton
3. Ft. McKinley
4. Vandalia
5. Englewood
6. Clayton
7. W. Milton
8. Laura
9. Lanuis
10. Troy
11. Piqua
12. St. Paris
13. New Carlisle
14. Springfield
15. Fairborn
16. Zimmerman
17. Xenia
18. Cedarville
19. S. Charleston
20. S. Solon
21. Jamestown
22. W. Lancaster
23. Bloomington
24. Wilmington
25. Gurneyville
26. New Burlington
27. Spring Valley
28. Bellbrook
29. Centerville
30. Jct. U. S. 48 & Ohio 73
31. Waynesville
32. Lebanon
33. Morrow
34. Midland
35. Blanchester
36. Hopkinsville
37. Pleasant Plain
38. Milford
39. Reading
40. Port Union
41. Ross
42. Hamilton
43. Princeton
44. Monroe
45. Franklin
46. Middletown
47. Jacksonburg
48. Sommerville
49. Oxford
50. Fairhaven
51. Boston
52. Eaton
53. Gratis
54. Farmersville
55. W. Alexandria
56. Lewisburg
57. New Paris
58. New Madison
59. Arcanum

Fig. 13.5—Environmental air sampling route.

tions by being physically isolated from other laboratory buildings, by permitting only essential traffic to and from other laboratories, by providing special clean laboratory clothing, and by requiring access to the laboratory through an air lock and a change house.

Low-resolution parallel-plate alpha counters are used for counting low-level alpha samples. These counters are being supplanted by windowless gas-flow proportional counters which have better long-time stability than the parallel-plate counter, and in addition have a very low background count and greater counting versatility owing to their short resolving time and large-area sample holder.

Proportional counters designed specifically for counting air samples deposited on filter paper of various sizes are also employed in health physics counting. These counters are connected to integrating pulse-rate meters which indicate the average counting rate directly on a calibrated meter. These counters are generally of the gas-flow type which are more stable and dependable than air proportional counters.

REFERENCES

1. W. F. Bale, D. L. Woernley, and L. B. Silverman, meeting with W. F. Bale, Report MLM-44-1-57, Jan. 28, 1944.
2. K. Z. Morgan, letter to R. S. Stone, Report MLM-45-12-81, Dec. 20, 1945.
3. R. M. Fink, editor, "Biological Studies with Polonium, Radium, and Plutonium," National Nuclear Energy Series, Division VI, Volume 3, pp. 35-153, McGraw-Hill Book Company, Inc., New York, 1950.
4. E. C. McCarthy, Pilot Laboratory, Dry-boxed Process Line, Report MLM-46-7-48, July 15, 1946; J. J. Burbage, A General Purpose Dry Box, Report MLM-48-3-47, Mar. 22, 1948.
5. L. B. Silverman, Excretion Activity Analyses as a Monitor for Polonium Exposures, Final Report No. 10, Report MLM-M-1443, Nov. 30, 1944.
6. E. S. Spoerl, Urine Assay Procedure at the Mound Laboratory, Report MLM-460, Apr. 14, 1950.
7. J. E. Bradley, Recommendation for Reduction of Mound Laboratory Environmental Survey Program, Report MLM-52-2-112, Feb. 25, 1953.
8. Basic Operating Procedures for Environmental Survey Samples, Report MLM-54-4-41, January 1948.

Appendix A

OBSERVED LINES OF Po

Intensity†	Occurrence‡	λ, A	ν (K)	Classification
35 ?	a,d	9,374.80	10,663.9	
250	a	9,227.87	10,833.8	
15 ?	a	9,051.9	11,044	
500	a,d	8,618.26	11,600.1	? $6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 7p\ ^5P_1$
150	a,d	8,506.04	11,753.1	
300	a,d	8,433.81	11,853.8	? $6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 7p\ ^5P_2$
50	a,d	8,193.0	12,202	
600	a,d	7,962.5	12,555	? $6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 7p\ ^5P_3$
15	a	7,648.44	13,071.0	
100	a	7,391.56	13,525.2	
35	a	7,373.48	13,558.4	
25	a	7,314.82	13,667.1	
10	a	7,311.84	13,672.7	
25	a	7,236.44	13,815.2	
20	a,d	6,245.5	16,007	
75	a	5,939.57	16,831.6	
300	a	5,744.77	17,402.3	$6p^4\ ^1D_2' - 6p^3\ (^4S^0)\ 7s\ ^5S_2^0$
100	a	5,388.87	18,551.6	$6p^3\ (^4S^0)\ 7s\ ^3S_1^0 - 6p^3\ (^4S^0)\ 8p\ 10_1$ or 10_2
300	a	5,323.40	18,779.8	$6p^3\ (^4S^0)\ 7s\ ^3S_1^0 - 6p^3\ (^4S^0)\ 8p\ 12_1$ or 12_2
100	a	5,236.32	19,092.1	
50	a	5,227.64	19,123.8	$6p^4\ ^1D_2' - 6p^3\ (^4S^0)\ 7s\ ^3S_1^0$
100	a	5,062.09	19,749.2	
450	a	4,946.91	20,209.0	
100	a	4,931.34	20,272.8	$6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 8p\ 10_1$ or 10_2
400	a	4,876.28	20,501.7	$6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 8p\ 12_1$ or 12_2
200	a,c	4,867.17	20,540.1	
50 h	c,d	4,825.91	20,715.7	
35 h	c,d	4,780.47	20,912.6	
50 h	c,d	4,684.68	21,340.2	
350	a	4,611.45	21,679.1	
100	a	4,564.69	21,901.1	$6p^3\ (^4S^0)\ 7s\ ^3S_1^0 - 6p^3\ (^4S^0)\ 9p\ 14_1$ or 14_2
175	a	4,543.48	22,003.4	$6p^3\ (^4S^0)\ 7s\ ^3S_1^0 - 6p^3\ (^4S^0)\ 9p\ 15_1$ or 15_2
50	a	4,513.3	22,151	
800	a,c	4,493.13	22,250.0	$6p^4\ ^3P_1 - 6p^3\ (^4S^0)\ 7s\ ^5S_2^0$
200 h	c,d	4,415.58	22,640.7	

Appendix A — (Continued)

Intensity†	Occurrence‡	λ, A	ν (K)	Classification
60	a,b	4,388.93	22,778.2	
20	b,d	4,381.13	22,818.8	
15	b	4,379.70	22,826.2	
50 ?	c,d	4,350.89	22,977.3	
50 ?	c,d	4,350.06	22,981.7	
20	b,d	4,319.76	23,142.9	
150	a,b	4,287.48	23,317.2	
50	a	4,274.95	23,385.6	
250	a,b	4,236.13	23,599.8	
60	a	4,232.00	23,622.9	$6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 9p\ 14_1$ or 14_2
30	a	4,227.35	23,648.9	$6p^3\ (^4S^0)\ 7s\ ^3S_1^0 - 6p^3\ (^4S^0)\ 10p\ 18_1$ or 18_2
125	a,b	4,213.73	23,725.3	$6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 9p\ 15_1$ or 15_2
20	b	4,187.75	23,872.5	
1,200	a,b	4,170.45	23,971.5	$6p^4\ ^3P_1 - 6p^3\ (^4S^0)\ 7s\ ^3S_1^0$
25	b,d	4,132.52	24,191.5	
50	b	4,078.29	24,513.2	
5	b,d	4,065.79	24,588.6	
200	b	4,051.98	24,672.3	
15	b,d	4,023.27	24,848.4	
150	b	3,963.35	25,224.1	
100	a,b	3,950.05	25,309.0	
25	a	3,948.84	25,316.8	
35	a	3,940.58	25,369.8	$6p^3\ (^4S^0)\ 7s\ ^5S_2^0 - 6p^3\ (^4S^0)\ 10p\ 18_1$ or 18_2
35	b,d	3,891.95	25,686.8	
150	b	3,884.93	25,733.2	
75	b	3,881.91	25,753.2	
75	b	3,866.66	25,854.8	
500	a,b	3,861.93	25,886.5	
40	b	3,752.31	26,642.7	
75	b	3,736.25	26,757.3	
75	b	3,682.56	27,147.3	
200	a,b	3,671.36	27,230.1	
50	a,b	3,615.72	27,649.1	
400	a,b	3,568.33	28,016.4	
40	b	3,551.09	28,152.4	
60	a,b	3,538.70	28,250.9	
35	b	3,520.36	28,398.1	
200	a,b,c	3,493.65	28,615.2	
300	a,b	3,489.79	28,646.9	
75	a,b	3,481.89	28,711.9	
150	a,b	3,472.75	28,787.4	
75	a,b	3,472.21	28,791.9	
25	b,c	3,453.49	28,948.0	
150 h	c,d	3,438.49	29,074.2	
100	a,b	3,436.59	29,090.3	

Appendix A — (Continued)

Intensity†	Occurrence‡	λ, A	ν (K)	Classification
50	a,b,c	3,433.0	29,121	
75	a,b	3,431.15	29,136.4	
25	a,b,c	3,404.8	29,362	
50	a,b	3,398.49	29,416.4	
175	a,b,c	3,396.35	29,435.0	
100	a,b	3,382.43	29,556.1	
10	a,b	3,381.58	29,563.5	
20	a,b	3,373.29	29,636.2	
25	a,b	3,365.47	29,705.0	
10	a,b	3,364.67	29,712.1	
35	a,d	3,346.66	29,872.0	
75	a,b	3,342.39	29,910.2	
600	a,b,c	3,328.61	30,034.0	$6p^4\ {}^1D'_2 - 1^0_2$
100	a,b	3,319.77	30,114.0	
250	a,b	3,286.39	30,419.8	$6p^4\ {}^1D'_2 - 2^0_3$
50	a,b	3,283.90	30,442.9	
20	a,d	3,283.62	30,445.4	
50	a,b	3,283.10	30,450.3	
10	a,b	3,280.26	30,476.7	
20	b,d	3,260.06	30,665.5	
50	a,b	3,257.62	30,688.4	
600	a,b,c	3,240.23	30,853.1	$6p^4\ {}^1D'_2 - 3^0_1$
400	a,b	3,189.01	31,348.7	$6p^4\ {}^1D'_2 - 4^0_2$
200	a,b	3,115.95	32,083.7	
450	a,b,c	3,069.29	32,571.4	$6p^4\ {}^1D'_2 - 5^0_1$
150	a,c	3,048.64	32,792.0	
50	c,d	3,034.26	32,947.4	
2,500 w	a,c	3,003.21	33,288.0	$6p^4\ {}^3P'_0 - 6p^3\ ({}^4S^0)\ 7s\ {}^3S^0_1$
600	a,c	2,958.90	33,786.5	$6p^4\ {}^1D'_2 - 6^0_2$
400	a,c	2,919.31	34,244.7	$6p^4\ {}^1D^2_2 - 7^0_2$
125	a	2,890.25	34,589.0	$6p^4\ {}^1D'_2 - 8^0_1$
300	a,c	2,866.01	34,881.5	$6p^4\ {}^3P_1 - 1^0_2$
250	a,c	2,824.13	35,398.7	$6p^4\ {}^1D'_2 - 9^0_1$
400	a,c	2,800.24	35,700.7	$6p^4\ {}^3P_1 - 3^0_1$
100	a	2,777.90	35,987.8	
600	a,c	2,761.91	36,196.2	$6p^4\ {}^3P_1 - 4^0_2$
200	a,c	2,671.69	37,418.3	$6p^4\ {}^3P_1 - 5^0_1$
700 h	c,d	2,663.33	37,535.8	
300	a,c	2,645.36	37,790.8	$6p^4\ {}^1D'_2 - 11^0_2$
200	a	2,637.03	37,910.2	
400	a,c	2,587.63	38,633.9	$6p^4\ {}^3P_1 - 6^0_2$
100 h	c,d	2,583.54	38,695.0	
300	a,c	2,578.79	38,766.3	
400	a,c	2,562.31	39,015.6	

Appendix A — (Continued)

Intensity†	Occurrence‡	λ, A	ν (K)	Classification
1,500 w	a,c	2,558.01	39,081.2	$6p^4\ {}^3P'_2 - 6p^3\ ({}^4S^0)\ 7s\ {}^5S^0_2$
300	a,c	2,557.33	39,091.6	$6p^4\ {}^3P_1 - 7^0_2$
300	a,c	2,534.95	39,436.7	$6p^4\ {}^3P_1 - 8^0_1$
150	a	2,534.19	39,448.5	
200 h	c,d	2,502.18	39,953.1	
700	a,c	2,490.56	40,139.5	$6p^4\ {}^1D'_2 - 13^0_1$ or 13^0_2
700	a,c	2,483.97	40,246.0	$6p^4\ {}^3P_1 - 9^0_1$
150 h	c,d	2,473.85	40,410.6	
1,500 w	a,c	2,450.11	40,802.1	$6p^4\ {}^3P'_2 - 6p^3\ ({}^4S^0)\ 7s\ {}^3S^0_1$
300	a	2,426.13	41,205.4	$6p^4\ {}^1D'_2 - 16^0_1$ or 16^0_2
250	a	2,421.74	41,280.1	$6p^4\ {}^1D'_2 - 17^0_1$ or 17^0_2
250	a	2,344.63	42,637.6	$6p^4\ {}^3P_1 - 11^0_2$
7	a	2,336.42	42,787.4	
50	a	2,325.39	42,990.3	
200	a	2,284.22	43,765.1	
200	a,c	2,222.14	44,987.6	$6p^4\ {}^3P_1 - 13^0_1$ or 13^0_2
300	a,c	2,220.67	45,017.4	$6p^4\ {}^3P'_0 - 3^0_1$
300 h	a,c	2,203.80	45,362.0	
30	a	2,170.71	46,053.5	$6p^4\ {}^3P'_1 - 16^0_1$ or 16^0_2
2	a	2,167.22	46,127.7	$6p^4\ {}^3P_1 - 17^0_1$ or 17^0_2
30 h	c,d	2,158.94	46,304.5	
10	a	2,153.37	46,424.3	
250 w	a,c	2,139.01	46,735.9	$6p^4\ {}^3P'_0 - 5^0_1$
100	a,c	2,050.48	48,753.5	$6p^4\ {}^3P'_0 - 8^0_1$
35	a	2,016.97	49,563.4	$6p^4\ {}^3P'_0 - 9^0_1$

Intensity	Occurrence‡	λ_{vac}, A	ν (K)	Classification
5	b,c	1,942.2	51,488	
5	a,d	1,933.8	51,712	$6p^4\ {}^3P'_2 - 1^0_2$
3	a,d	1,919.4	52,100	$6p^4\ {}^3P'_2 - 2^0_3$

† h = hazy, diffuse; w = wide; and ? = doubtful assignment to polonium.

‡ Under occurrence, a signifies observation in the low-frequency electrodeless discharge, b denotes observation in the high-frequency electrodeless discharge, c represents observation in the spark discharge, and d means that the line was measured on only one spectrogram.

Appendix B

ENERGY LEVELS OF Po I

Configuration	Level notation	Relative value (K)	Comments
$6p^4$	$^3P'_2$	0	
$6p^4$	$^3P'_0$	7,514	
$6p^4$	$^3P_1$	16,831	
$6p^4$	$^1D'_2$	21,679	
$6p^3$ ($^4S^0$) 7s	$^5S^0_2$	39,081	
$6p^3$ ($^4S^0$) 7s	$^3S^0_1$	40,802	
	1^0_2	51,712	
	2^0_3	52,099	
	3^0_1	52,532	
	4^0_2	53,027	
	5^0_1	54,250	
	6^0_2	55,465	
	7^0_2	55,923	$6p^3$ ($^4S^0$) 8s $^5S^0_2$?
	8^0_1	56,268	$6p^3$ ($^4S^0$) 8s $^3S^0_1$?
	9^0_1	57,077	
$6p^3$ ($^4S^0$) 8p ?	10_1 or 10_2	59,354	
	11^0_2	59,469	
$6p^3$ ($^4S^0$) 8p ?	12_1 or 12_2	59,583	
	13^0_1 or 13^0_2	61,818	
$6p^3$ ($^4S^0$) 9p ?	14_1 or 14_2	62,704	
$6p^3$ ($^4S^0$) 9p ?	15_1 or 15_2	62,806	
	16^0_1 or 16^0_2	62,884	
	17^0_1 or 17^0_2	62,959	
$6p^3$ ($^4S^0$) 10p ?	18_1 or 18_2	64,551	

Appendix C

OBSERVED BAND HEADS OF POLONIUM

Molecule Po^{208} Po^{208}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
2	3,552.3	28,143	1	3,553.4	28,134
3	3,562.0	28,066	2	3,563.0	28,058
4	3,571.9	27,988	3	3,573.0	27,980
4	3,581.6	27,913	4	3,582.7	27,904
4	3,591.4	27,836	4	3,592.5	27,828
4	3,601.4	27,759	3	3,602.3	27,752
4	3,611.3	27,683	1 ?	3,612.3	27,675
0	3,644.1	27,434	0	3,645.0	27,427
0	3,645.6	27,423	0	3,646.7	27,414
0	3,647.8	27,406	0	3,648.9	27,398
1	3,656.9	27,338	1	3,658.3	27,327
1	3,659.3	27,320	1	3,660.6	27,310
0	3,666.2	27,268	0	3,667.3	27,260
1	3,668.6	27,251	2	3,669.6	27,243
2	3,671.2	27,231	4	3,672.2	27,224
0	3,674.1	27,210	1	3,675.0	27,203
1	3,680.2	27,165	1	3,681.1	27,158
3	3,683.0	27,144	4	3,684.1	27,136
1	3,686.3	27,120	1	3,687.4	27,112
2	3,692.1	27,077	2	3,693.0	27,071
3	3,695.2	27,054	3	3,696.2	27,047
3	3,698.9	27,027	3	3,699.7	27,022
1	3,704.2	26,989	1	3,704.9	26,984
3	3,707.7	26,963	5	3,708.7	26,956
2	3,711.3	26,937	4	3,712.3	26,930
4	3,720.3	26,872	4	3,721.2	26,865
2	3,724.2	26,844	4	3,725.3	26,836
2	3,732.9	26,781	2	3,733.9	26,774
3	3,737.3	26,750	3	3,738.3	26,743
2	3,745.9	26,688	2	3,747.0	26,680
5	3,750.5	26,656	5	3,751.5	26,648
3	3,759.4	26,592	2	3,760.4	26,585
4	3,764.1	26,559	3	3,765.1	26,552
3	3,777.9	26,462	4	3,778.8	26,456
4	3,791.9	26,365	4	3,792.7	26,359

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
2	3,795.1	26,342	1 ?	3,795.3	26,341
3	3,806.1	26,266	4	3,806.9	26,261
2	3,809.0	26,246	1	3,809.4	26,243
5	3,820.6	26,167	4	3,821.3	26,162
3	3,822.8	26,151	1	3,823.5	26,147
0	3,834.4	26,072			
4	3,835.4	26,066	2	3,835.9	26,062
1	3,837.2	26,053	1	3,838.0	26,048
1	3,840.0	26,034	1	3,840.5	26,031
3	3,843.5	26,011	2	3,844.1	26,007
3	3,850.2	25,965	2	3,850.8	25,961
1 ?	3,851.8	25,955	1	3,852.5	25,950
2	3,854.1	25,939	2	3,854.5	25,936
5	3,858.4	25,910	3	3,858.8	25,907
3	3,865.4	25,863	2	3,865.9	25,860
2	3,868.4	25,843	1	3,869.0	25,839
1	3,871.0	25,826	1 ?	3,871.7	25,821
5	3,873.5	25,809	4	3,874.0	25,806
4	3,874.9	25,800	3	3,875.3	25,797
1	3,881.0	25,759	1 ?	3,881.3	25,757
0	3,883.2	25,745			
2	3,885.4	25,730	1	3,885.8	25,727
5	3,888.9	25,707	3	3,889.3	25,704
4	3,889.9	25,700	2	3,890.3	25,698
0	3,892.4	25,684			
1	3,896.8	25,655	1	3,897.3	25,652
2	3,900.0	25,634	1	3,900.3	25,632
6	3,904.5	25,604	4	3,904.8	25,602
2	3,905.2	25,600	4	3,905.5	25,598
5	3,906.4	25,592	4	3,906.7	25,590
1	3,911.3	25,560			
3	3,912.6	25,551	2	3,912.8	25,550
5	3,920.4	25,500	5	3,920.6	25,499
2	3,921.5	25,493	4	3,921.7	25,492
7	3,928.3	25,449	5	3,928.6	25,447
2	3,931.7	25,427	1	3,931.8	25,426
5	3,936.6	25,395	3	3,936.8	25,394
2	3,938.3	25,385	2	3,938.3	25,385
8	3,944.4	25,345	7	3,944.5	25,345
3	3,953.4	25,288	2	3,953.3	25,288
1	3,957.7	25,260	1	3,957.4	25,262
10	3,960.6	25,242	8	3,960.7	25,241
5	3,968.6	25,191	4	3,968.6	25,191
1	3,970.2	25,181	1	3,970.1	25,181
4	3,976.5	25,141	3	3,976.5	25,141
5	3,977.3	25,136	6	3,977.3	25,136
3	3,984.4	25,091	2 ?	3,984.6	25,090
6	3,985.1	25,086	6	3,985.0	25,087
3	3,992.6	25,039	3	3,992.7	25,039
2	3,994.2	25,029	1	3,994.2	25,029

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A.	Frequency (K)
1 ?	3,996.0	25,018	1	3,995.8	25,019
4	4,000.8	24,988	3	4,000.7	24,989
7	4,001.9	24,981	7	4,001.7	24,982
	4,004.5	24,965			
2	4,008.6	24,939	1	4,008.4	24,941
2	4,009.7	24,932	2	4,009.6	24,933
3	4,016.6	24,890	2	4,016.5	24,890
3	4,017.5	24,884	3	4,017.5	24,884
5	4,019.0	24,875	6	4,018.8	24,876
4	4,025.2	24,836	3	4,025.1	24,837
6	4,026.4	24,829		4,026.4	24,829
6	4,026.6	24,828			
4	4,033.2	24,787	3	4,033.0	24,788
2	4,036.4	24,768	2	4,036.0	24,770
2	4,041.2	24,738	2	4,040.9	24,740
3	4,042.1	24,733	3	4,041.9	24,734
5	4,044.0	24,721	6	4,043.6	24,723
			2	4,046.5	24,706
2	4,049.3	24,689	1	4,049.0	24,691
3	4,050.3	24,683	0 ?	4,049.9	24,685
4	4,051.7	24,674	1	4,051.1	24,678
7	4,057.9	24,636	5	4,057.5	24,639
4	4,059.4	24,627	1	4,058.9	24,630
8	4,061.6	24,614	3	4,061.0	24,618
2	4,063.6	24,602	0 ?	4,063.4	24,603
3	4,066.1	24,587	2	4,065.6	24,590
2	4,067.1	24,581	0 ?	4,066.7	24,583
10	4,069.1	24,569	7	4,068.7	24,571
2	4,073.9	24,540	1	4,073.3	24,543
3	4,074.9	24,534	3	4,074.5	24,536
1	4,079.4	24,507	1	4,079.0	24,509
3	4,082.1	24,490	2	4,081.5	24,494
6	4,084.5	24,476	4	4,084.0	24,479
10	4,086.9	24,462	8	4,086.4	24,465
4	4,090.8	24,438	3	4,090.2	24,442
2	4,091.6	24,433			
3	4,094.4	24,417	5	4,094.0	24,419
2	4,098.8	24,391	1	4,098.2	24,395
4	4,100.0	24,383	2	4,099.4	24,387
2	4,100.8	24,379			
2	4,102.0	24,371	1	4,101.5	24,374
3	4,105.0	24,354	2	4,104.4	24,357
2	4,106.6	24,344	1	4,106.0	24,348
2	4,107.9	24,336	1	4,107.3	24,340
3	4,109.8	24,325	2	4,109.1	24,329
1	4,111.3	24,316			
10	4,112.4	24,310	7	4,111.9	24,313
4	4,115.1	24,294	2	4,114.2	24,299
8	4,117.5	24,280	4	4,116.9	24,283
0 ?	4,121.6	24,256			

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
4	4,123.8	24,243	2	4,122.9	24,248
3	4,124.5	24,239			
7	4,127.7	24,220	3	4,126.7	24,226
5	4,130.9	24,201	5	4,130.1	24,206
3	4,131.8	24,196	0 ?	4,131.0	24,200
6	4,133.1	24,188	2	4,132.5	24,192
8	4,138.3	24,158	6	4,137.6	24,162
2	4,139.5	24,151	0 ?	4,138.8	24,155
2	4,140.9	24,143			
4	4,143.0	24,130	2	4,142.3	24,134
			?	4,143.7	24,126
3	4,148.0	24,101	2	4,147.1	24,106
1	4,148.8	24,097			
2	4,150.7	24,086	1	4,150.1	24,089
3	4,153.4	24,070	3	4,152.5	24,075
				4,153.9	24,067
10	4,156.9	24,050	8	4,156.0	24,055
2	4,161.1	24,025	2	4,160.1	24,031
3	4,164.2	24,007	2	4,163.5	24,012
2	4,165.2	24,002			
3	4,166.4	23,995	3	4,165.4	24,001
3	4,176.5	23,937	1	4,175.7	23,941
1	4,179.6	23,919			
2	4,181.4	23,909	0 ?	4,180.5	23,914
8	4,183.2	23,898	3	4,182.2	23,904
5	4,187.1	23,876	2	4,185.8	23,884
3	4,190.5	23,857	2	4,189.5	23,862
6	4,198.0	23,814	2	4,197.0	23,820
4	4,200.0	23,803	1	4,198.8	23,810
2	4,202.2	23,790	0	4,201.3	23,795
10	4,209.5	23,749	5	4,208.5	23,755
			3	4,209.1	23,751
			1	4,211.9	23,736
1	4,214.9	23,719			
3	4,220.8	23,686	2	4,219.6	23,692
0 ?	4,223.2	23,672			
6	4,224.3	23,666	3	4,223.2	23,672
3	4,232.0	23,623	2	4,230.6	23,631
2	4,233.7	23,613	1	4,232.6	23,620
6	4,236.1	23,600	5	4,235.0	23,606
3	4,243.8	23,557	3	4,242.7	23,563
2	4,247.2	23,538	2	4,245.9	23,546
2	4,254.8	23,496	1	4,253.6	23,503
4	4,258.5	23,476	2	4,257.2	23,483
6	4,263.3	23,449	4	4,261.7	23,458
2	4,266.1	23,434	1	4,265.1	23,440
2	4,267.8	23,425	2	4,266.6	23,431
6	4,270.5	23,410	3	4,269.0	23,418
3	4,278.2	23,368	2	4,276.7	23,376
1	4,281.3	23,351	2	4,279.8	23,359

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
2	4,285.4	23,329	3	4,283.8	23,337
3	4,290.5	23,301	4	4,288.9	23,309
1	4,291.6	23,295			
3	4,292.8	23,288	2	4,291.5	23,295
4	4,297.7	23,262	5	4,296.1	23,270
1	4,300.4	23,247	1	4,298.8	23,256
1	4,302.1	23,238	1	4,300.4	23,247
1	4,304.7	23,224	1	4,303.1	23,233

Molecule Po^{208} Po^{208}			Molecule Po^{208} Po^{209}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
1	4,310.1	23,195				0 ?	4,308.4	23,204
3	4,312.4	23,182				2	4,310.7	23,192
2	4,315.7	23,165				2	4,313.9	23,174
2	4,317.8	23,153				3	4,316.0	23,163
3	4,319.8	23,143				2	4,318.1	23,152
1	4,323.3	23,124						
5	4,325.0	23,115				5	4,323.2	23,125
2	4,327.4	23,102				2	4,325.4	23,113
2	4,332.4	23,075				3	4,330.6	23,085
1	4,334.1	23,066				0	4,332.5	23,075
1	4,342.6	23,021				2	4,340.7	23,031
0	4,345.5	23,006				1	4,343.4	23,017
0 ?	4,346.9	22,998				2	4,345.1	23,008
1	4,350.2	22,981				2	4,348.2	22,992
3	4,352.4	22,969				5	4,350.4	22,980
3	4,354.4	22,959				4	4,352.6	22,968
1	4,359.7	22,931				6	4,357.7	22,941
0	4,361.8	22,920				1	4,360.1	22,929
1	4,367.1	22,892				2	4,364.9	22,904
0 ?	4,368.4	22,885				1	4,366.0	22,898
0 ?	4,370.8	22,873				1	4,368.7	22,884
1	4,373.0	22,861				2	4,371.1	22,871
1	4,377.2	22,839	0	4,376.8	22,841	3	4,375.1	22,850
0	4,379.0	22,830				1	4,376.7	22,842
1	4,380.2	22,824				5	4,378.1	22,835
3	4,381.3	22,818				2	4,379.0	22,830
2 ?	4,382.0	22,814				3	4,379.7	22,826
1	4,384.8	22,800				2	4,382.6	22,811
4	4,387.4	22,786	0 ?	4,386.9	22,789	6	4,385.1	22,798
3	4,389.3	22,776				4	4,386.9	22,789
0	4,392.6	22,759				1	4,390.4	22,771
2	4,394.6	22,749				3	4,392.3	22,761
1	4,396.9	22,737				0 ?	4,394.5	22,749
0	4,408.1	22,679	0 ?	4,407.7	22,681	3	4,405.8	22,691
0	4,409.4	22,672						

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{208} Po^{209}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
0	4,411.9	22,660	0 ?	4,411.3	22,663	2	4,409.6	22,671
2	4,415.2	22,643	0	4,414.7	22,645	3	4,412.9	22,654
1	4,416.1	22,638				1	4,413.7	22,650
2	4,416.8	22,634				3	4,414.5	22,646
1	4,419.1	22,623				2	4,417.3	22,632
2	4,422.6	22,605	0	4,421.9	22,608	3	4,420.1	22,618
2	4,424.2	22,597				3	4,421.8	22,609
1	4,429.7	22,569				2	4,427.3	22,581
0	4,431.6	22,559				1	4,429.4	22,570
2	4,436.0	22,537				1	4,433.7	22,548
3	4,443.4	22,499	0 ?	4,442.8	22,502	3	4,440.9	22,512
0	4,446.6	22,483				1	4,444.2	22,495
0	4,448.1	22,475				0	4,445.8	22,487
4	4,450.5	22,463	0	4,449.9	22,466	7	4,448.0	22,476
						3	4,448.5	22,473
2	4,451.9	22,456				5	4,449.4	22,469
1	4,454.6	22,442				2	4,452.2	22,455
2	4,457.7	22,427				6	4,455.3	22,439
3	4,459.2	22,419				4	4,457.2	22,429
1	4,462.4	22,403				1	4,459.8	22,416
2	4,464.9	22,391				3	4,462.5	22,403
1	4,466.8	22,381				2	4,464.3	22,394
2	4,471.5	22,358				3	4,469.0	22,370
2	4,478.7	22,322	0	4,478.2	22,324	5	4,476.1	22,335
						0	4,480.7	22,312
4	4,485.9	22,286	1	4,485.2	22,289	6	4,483.3	22,299
2	4,487.2	22,279				2	4,484.5	22,293
2	4,489.8	22,266				2	4,487.3	22,279
						3	4,490.6	22,263
2	4,500.3	22,215				3	4,497.7	22,227
?	4,502.0	22,206				2	4,499.3	22,219
						0	4,502.8	22,202
2	4,507.2	22,181	0	4,506.6	22,183	3	4,504.3	22,195
2	4,514.3	22,146	?	4,513.6	22,149	3	4,511.4	22,160
2	4,521.3	22,111	0	4,520.5	22,115	3	4,518.7	22,124
?	4,521.8	22,109						
1	4,522.6	22,105				1	4,519.8	22,119
						0	4,523.8	22,099
4	4,528.7	22,075	0	4,528.1	22,078	5	4,525.8	22,089
2	4,529.9	22,069				5	4,527.1	22,083
1	4,532.8	22,055				2	4,530.0	22,069
2	4,535.9	22,040	0	4,535.3	22,043	4	4,533.1	22,054
2	4,537.5	22,032				4	4,534.7	22,046
0	4,540.8	22,016				1	4,538.0	22,030
5	4,543.2	22,005	0	4,542.5	22,008	4	4,540.0	22,020
2	4,550.1	21,971	0	4,549.3	21,975	3	4,547.1	21,986
3	4,557.3	21,937	0	4,556.5	21,941	3	4,554.3	21,951
0	4,558.2	21,932				2	4,555.1	21,947
3	4,564.6	21,902	0	4,563.7	21,906	4	4,561.5	21,916
1	4,565.6	21,897				4	4,562.6	21,911

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{208} Po^{209}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
?	4,568.3	21,884				2	4,565.1	21,899
2	4,571.9	21,867	0	4,571.1	21,870	3	4,568.7	21,882
1	4,573.1	21,861	0	4,572.5	21,864	3	4,570.1	21,875
0	4,576.4	21,845				1	4,573.2	21,860
						0	4,574.5	21,854
2	4,578.9	21,833				4	4,575.7	21,848
1	4,580.8	21,824				2	4,577.7	21,839
3	4,586.0	21,799	0	4,585.2	21,803	3	4,582.9	21,814
3	4,593.1	21,766	1	4,592.3	21,770	3	4,590.0	21,780
						1	4,590.9	21,776
3	4,600.3	21,732	1	4,599.5	21,735	3	4,597.1	21,747
2	4,601.2	21,727				2	4,598.0	21,743
3	4,607.8	21,696				2	4,604.5	21,712
3	4,608.7	21,692				2	4,605.7	21,706
3	4,614.9	21,663	1	4,614.1	21,667	3	4,611.6	21,678
2	4,616.3	21,656				2	4,613.0	21,672
3	4,622.0	21,630	0	4,621.3	21,633	3	4,618.6	21,646
3	4,629.1	21,596	1	4,628.3	21,600	3	4,625.7	21,612
3	4,636.3	21,563	1	4,635.5	21,567	2	4,632.9	21,579
2	4,637.1	21,559				2	4,633.7	21,575
						1	4,636.7	21,561
2	4,643.6	21,529	0	4,642.6	21,534	2	4,640.1	21,545
2	4,644.6	21,524				2	4,641.2	21,540
0	4,647.9	21,509				0	4,644.1	21,527
2	4,651.1	21,494				2	4,647.5	21,511
2	4,652.2	21,489				1	4,648.7	21,505
						0	4,653.0	21,486
3	4,658.1	21,462	0	4,657.3	21,466	3	4,654.6	21,478
1	4,659.9	21,454				1	4,656.4	21,470
3	4,665.2	21,429	1	4,664.4	21,433	3	4,661.7	21,445
4	4,672.4	21,396	1	4,671.6	21,400	3	4,668.8	21,413
						1	4,669.4	21,410
3	4,679.7	21,363	1	4,678.8	21,367	1	4,676.0	21,380
3	4,680.5	21,359				2	4,676.7	21,377
						0	4,679.5	21,364
2	4,687.4	21,328				2	4,683.5	21,346
1	4,688.1	21,325				2	4,684.4	21,341
0	4,691.0	21,311				0	4,687.2	21,329
3	4,694.5	21,296	1	4,693.5	21,300	2	4,690.8	21,312
2	4,695.7	21,290				1	4,692.0	21,307
4	4,701.5	21,264	1	4,700.6	21,268	3	4,697.8	21,281
3	4,708.6	21,232	1	4,707.7	21,236	3	4,704.9	21,249
1	4,709.8	21,226				1	4,706.2	21,243
3	4,715.9	21,199	1	4,714.9	21,203	1	4,712.1	21,216
3	4,716.8	21,195				2	4,713.0	21,212
3	4,724.0	21,163				2	4,720.0	21,181
3	4,730.8	21,132	0	4,729.8	21,137	2	4,727.0	21,149
1	4,731.8	21,128				1	4,727.9	21,145
0 ?	4,734.7	21,115				0	4,730.8	21,132
3	4,737.9	21,101	1	4,736.9	21,105	3	4,734.0	21,118

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{208} Po^{209}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
2	4,739.5	21,093				1	4,735.7	21,110
3	4,744.9	21,069	1	4,744.0	21,073	3	4,741.1	21,086
3	4,752.1	21,037	1	4,751.2	21,041	2	4,748.2	21,055
1	4,753.4	21,032				1	4,749.3	21,050
2	4,759.4	21,005	1	4,758.3	21,010	1	4,755.4	21,023
3	4,760.2	21,002				3	4,756.2	21,019
3	4,767.2	20,971				1	4,763.2	20,988
						1	4,763.8	20,986
0	4,770.6	20,956				0	4,766.6	20,973
3	4,774.2	20,940	1	4,773.1	20,945	2	4,770.2	20,958
1	4,775.3	20,935				1	4,771.4	20,952
0	4,778.5	20,921				0	4,774.3	20,940
3	4,781.3	20,909	1	4,780.3	20,913	2	4,777.3	20,926
1	4,783.2	20,901				0	4,779.0	20,919
0	4,786.3	20,887						
3	4,788.4	20,878	0	4,787.3	20,883	2	4,784.3	20,896
2	4,789.9	20,871				1	4,785.7	20,890
2	4,795.7	20,846	0 ?	4,794.6	20,851	0	4,791.5	20,864
1	4,796.7	20,846				1	4,792.5	20,860
3	4,803.7	20,811	1	4,802.9	20,815	2	4,799.6	20,829
2	4,810.8	20,781	0 ?	4,809.7	20,786	1	4,806.5	20,799
1	4,811.5	20,778				0	4,807.3	20,796
3	4,817.9	20,750	1	4,816.9	20,754	1	4,813.6	20,769
						0	4,815.0	20,763
2	4,825.0	20,720	0	4,823.9	20,724	1	4,820.6	20,739
2	4,832.0	20,690	0	4,831.0	20,694	1	4,827.7	20,708
1	4,833.6	20,683				0	4,829.2	20,702
1	4,839.3	20,658	0	4,838.2	20,663	0 ?	4,834.9	20,677
2	4,840.4	20,654				1	4,836.0	20,672
2	4,847.4	20,624	0 ?	4,846.5	20,628	2	4,843.0	20,643
2	4,854.3	20,595	0	4,853.1	20,600	1	4,849.8	20,614
0 ?	4,855.4	20,590				1	4,850.7	20,610
2	4,861.4	20,564	0	4,860.3	20,569	1	4,856.9	20,584
0	4,863.1	20,557				0	4,858.6	20,576
1	4,868.5	20,534				1	4,864.0	20,553
						0 ?	4,871.1	20,524
0	4,874.6	20,509						
2	4,883.0	20,474				0 ?	4,878.3	20,493
2	4,883.9	20,470				1	4,879.2	20,489
0 ?	4,890.3	20,443						
1	4,891.0	20,440				1	4,886.3	20,460
2	4,897.9	20,411	0	4,896.8	20,416	0	4,893.3	20,430
1	4,906.8	20,374				1	4,901.9	20,395
2	4,912.1	20,352	1	4,911.0	20,357	0	4,907.4	20,372
1	4,913.6	20,346				0	4,908.8	20,366
1	4,919.3	20,322	0 ?	4,918.4	20,326	0	4,914.4	20,343
1	4,920.6	20,317				1	4,915.8	20,337
1	4,926.4	20,293						
2	4,927.6	20,288				2	4,922.6	20,309
2	4,934.6	20,259				1	4,929.8	20,279

Appendix C — (Continued)

Molecule Po^{208} Po^{208}			Molecule Po^{208} Po^{209}			Molecule Po^{210} Po^{210}		
Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)	Intensity	Wavelength, A	Frequency (K)
3	4,941.4	20,231	1	4,940.2	20,236	1	4,936.6	20,251
1	4,948.3	20,203				1	4,943.5	20,223
0	4,950.4	20,195						
2	4,955.7	20,173	0 ?	4,954.5	20,178	0	4,950.8	20,193
1	4,957.0	20,168				0	4,952.3	20,187
1	4,964.1	20,139				1	4,959.1	20,159
1	4,971.0	20,111	0 ?	4,969.6	20,117	2	4,966.0	20,131
1	4,972.6	20,105						
2	4,978.0	20,083						
1	4,985.5	20,053	0	4,984.2	20,058	1 ?	4,980.1	20,074
1	4,986.4	20,049						
1	4,992.5	20,024	0	4,991.3	20,029	1	4,987.2	20,046
0	4,994.4	20,017						
0	4,998.5	20,000						
1	4,999.6	19,996				0	4,994.3	20,017
						0	4,998.8	19,999
						1	5,002.4	19,985
						1	5,009.3	19,957
						0	5,016.4	19,929
						1	5,023.2	19,902
						0	5,030.5	19,873
						1	5,045.4	19,815
						0	5,052.3	19,787
						0	5,066.3	19,733
						0	5,071.9	19,711
						1	5,095.1	19,621
						0	5,102.1	19,594
						1	5,109.5	19,566
						1 ?	5,131.2	19,483

Appendix D

VIBRATIONAL ENERGY LEVELS OF GROUND STATE OF Po_2^{210}

ν''	Observed level value (K)	Calculated level value (K)
0	0	0
1	156	155
2	309	310
3	463	464
4	617	617
5	769	770
6	921	922
7	1072	1073
8	1221	1223
9	1371	1373
10	1520	1522
11	1668	1670
12	1816	1818
13	1963	1965
14	2108	2111
15	2253	2256
16	2399	2401
17	2542	2545
18	2686	2688
19	2829	2830
20	2969	2972
21	3112	3113
22	3251	3253
23	3391	3393
24	3529	3532
25	3668	3670
26	3806	3808
27	3943	3944
28	4080	4080
29	4215	4215
30	4350	4350
31	4483	4484
32	4617	4617
33	4750	4749
34	4881	4881
35	5012	5012
36	5143	5142
37	5272	5272
38	5401	5401
39	5530	5529
40	5657	5656
41	5784	5783
42	5910	5909
43	6035	6034
44	6160	6158
45	6283	6282
46	6407	6406
47	6528	6527
48	6650	6649
49	6770	6770
50	6890	6890
51	7010	7009
52	7128	7128
53	7246	7246
54	7363	7363
55	7477	7480
56	(7592)	7596

Appendix E

VIBRATIONAL ENERGY LEVELS OF EXCITED STATE OF Po_2^{210} REFERRED TO LOWEST LEVEL OF GROUND STATE

Level	Observed value (K)	Calculated value (K)
0	25,125	25,125
1	25,233	25,233
2	25,340	25,339
3	25,446	25,465
4	25,550	25,550
5	25,654	25,654
6	25,757	25,758
7	25,860	25,860
8	25,961	25,961
9	26,062	26,062
10	26,162	26,162
11	26,260	26,261
12	26,359	26,359
13	26,455	26,456
14	26,551	26,553
15	26,647	26,648
16	26,741	26,743
17	26,835	26,837
18	26,932	26,930
19	27,023	27,022
20	27,112	27,113
21	27,204	27,203
22	27,294	27,293
23	27,380	27,382
24	27,469	27,469
25	27,554	27,556

Appendix F

COMPARISON OF OBSERVED AND CALCULATED ISOTOPE SHIFTS

		Po$_2^{208}$-Po$_2^{210}$		Po^{208} Po^{209}-Po$_2^{210}$	
Band	Frequency in Po$_2^{210}$ (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
4−0	25,550	1.9	1		
5−0 ?	25,652	2.4	3		
6−0	25,757	2.8	2		
7−0	25,860	3.3	3		
8−0	25,961	3.8	4		
9−0	26,062	4.2	4		
10−0	26,162	4.7	5		
11−0	26,261	5.1	5		
12−0	26,359	5.5	6		
13−0	26,456	5.9	6		
14−0	26,552	6.3	7		
15−0	26,648	6.7	8		
16−0	26,743	7.1	7		
17−0	26,836	7.5	8		
18−0	26,930	7.8	7		
19−0	27,022	8.2	5		
20−0	27,112	8.6	8		
21−0	27,203	8.9	7		
22−0	27,292	9.3	8		
24−0 ?	27,468	9.9			
25−0 ?	27,556	10.2			
2−1	25,181	0.2	0		
3−1	25,288	0.7	0		
4−1	25,394	1.2	1		
5−1	25,499	1.6	1		
6−1	25,602	2.1	2		
7−1	25,704	2.6	3		
8−1	25,806	3.1	3		
9−1	25,907	3.5	3		
10−1	26,007	3.9	4		

Appendix F — (Continued)

		Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
16−1 ?	26,585	6.3	7		
17−1	26,680	6.7	8		
18−1	26,774	7.1	7		
19−1	26,865	7.5	7		
20−1	26,956	7.8	7		
21−1	27,047	8.2	7		
22−1	27,136	8.5	8		
23−1	27,224	8.9	7		
24−1	27,310	9.2	10		
25−1 ?	27,398	9.5	8		
26−1 ?	27,485	9.8	8		
27−1 ?	27,568	10.1	10		
1−2 ?	24,925	1.1	1		
2−2	25,029	−0.6	0		
3−2	25,136	−0.1	0		
4−2	25,241	0.4	1		
5−2	25,345	0.9	0		
6−2	25,447	1.3	2		
7−2	25,550	1.8	1		
8−2	25,652	2.3	3		
12−2 ?	26,048	4.0	5		
13−2	26,147	4.4	4		
14−2	26,243	4.8	3		
15−2 ?	26,341	5.2	1		
20−2	26,804	7.1	3		
22−2	26,984	7.8	5		
23−2	27,071	8.1	6		
24−2	27,158	8.4	7		
25−2	27,243	8.7	8		
26−2	27,327	9.0	11		
27−2 ?	27,414	9.3	9		
28−2	27,498	9.6	7		
29−2	27,581	9.9	8		
1−3	24,770	−1.8	−2		
2−3	24,876	−1.3	−1		
3−3	24,982	−0.8	−1		
4−3	25,087	−0.3	1		
5−3	25,191	0.2	0		
6−3 ?	25,295	0.6	0		
8−3	25,499	1.5	1		
9−3	25,598	2.0	2		
10−3	25,698	2.5	2		

Appendix F—(Continued)

Band	Frequency in Po_2^{210} (K)	Po_2^{208}-Po_2^{210} Calculated (K)	Po_2^{208}-Po_2^{210} Observed (K)	Po^{208} Po^{209}-Po_2^{210} Calculated (K)	Po^{208} Po^{209}-Po_2^{210} Observed (K)
11−3	25,797	2.9	3		
16−3	26,280	4.8	5		
17−3 ?	26,375	5.2	1		
18−3 ?	26,469	5.6			
27−3	27,260	8.6	8		
28−3	27,344	8.9	8		
29−3	27,427	9.2	7		
30−3	27,509	9.5	8		
31−3	27,591	9.8	6		
0−4	24,509	−3.1	−2		
1−4	24,618	−2.5	−4		
2−4	24,723	−2.0	−2		
3−4	24,829	−1.5	0		
4−4	24,933	−1.0	−1		
5−4	25,039	−0.5	0		
6−4	25,141	0.0	0		
7−4 ?	25,241	0.4	1		
8−4	25,345	0.9	0		
9−4	25,447	1.3	2		
13−4	25,839	3.0	4		
14−4	25,936	3.4	3		
15−4	26,031	3.8	3		
21−4	26,585	6.0	7		
22−4	26,674	6.4	6		
23−4 ?	26,763	6.7	7		
24−4 ?	26,850	7.0	7		
0−5	24,357	−3.9	−3		
1−5	24,465	−3.3	−3		
2−5	24,571	−2.8	−2		
3−5	24,678	−2.3	−4		
5−5 ?	24,884	−1.4	0		
6−5	24,989	−1.0	1		
7−5 ?	25,090	−0.5	1		
8−5 ?	25,191	0.0	0		
10−5 ?	25,394	0.9	1		
11−5	25,492	1.4	1		
12−5	25,590	1.8	2		
24−5	26,698	6.2	6		
25−5	26,785	6.6			
0−6	24,206	−4.5	−5		
1−6	24,313	−4.0	−3		

Appendix F — (Continued)

		Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
2−6	24,419	−3.5	−2		
4−6	24,630	−2.5	−3		
5−6	24,734	−2.0	−1		
6−6	24,837	−1.5	−1		
7−6 ?	24,941	−1.1	−2		
9−6	25,141	−0.1	0		
10−6	25,241	0.4	1		
14−6	25,632	2.0	2		
15−6	25,727	2.4	3		
16−6	25,821	2.8	5		
18−6	26,007	3.5	4		
21−6	26,280	4.6	5		
0−7	24,055	−5.2	−5		
1−7	24,162	−4.6	−4		
3−7	24,374	−4.0	−3		
4−7	24,479	−3.3	−3		
5−7	24,583	−2.7	−2		
6−7	24,685	−2.2	−2		
7−7	24,788	−1.7	−1		
8−7	24,890	−1.3	0		
9−7	24,989	−0.8	−1		
10−7	25,090	−0.4	1		
12−7	25,288	0.5	0		
13−7	25,385	0.9	0		
16−7	25,670	2.0			
19−7	25,950	3.2	5		
0−8	23,909	−5.9	−6		
1−8	24,012	−5.4	−5		
3−8 ?	24,226	−4.4	−6		
4−8	24,329	−3.9	−4		
6−8	24,536	−2.9	−2		
7−8	24,639	−2.5	−3		
8−8	24,740	−2.0	−2		
9−8 ?	24,837	−1.6	−1		
15−8	25,426	0.9	1		
16−8	25,521	1.3	0		
18−8 ?	25,704	2.1	3		
19−8 ?	25,797	2.5	3		
0−9	23,755	−6.5	−6		
1−9	23,862	−5.9	−5		
3−9	24,075	−4.7	−5		

Appendix F — (Continued)

Band	Frequency in Po_2^{210} (K)	Po_2^{208}-Po_2^{210} Calculated (K)	Po_2^{208}-Po_2^{210} Observed (K)	Po^{208} Po^{209}-Po_2^{210} Calculated (K)	Po^{208} Po^{209}-Po_2^{210} Observed (K)
5−9	24,283	−4.1	−3		
6−9	24,387	−3.6	−4		
8−9	24,590	−2.7	−3		
9−9	24,691	−2.2	−2		
11−9	24,890	−1.4	0		
12−9 ?	24,989	−1.0	−1		
13−9 ?	25,087	−0.5	−1		
0−10	23,606	−7.2	−6		
2−10	23,820	−6.2	−6		
4−10	24,031	−5.2	−6		
5−10	24,134	−4.7	−4		
7−10	24,340	−3.7	−4		
8−10	24,442	−3.3	−4		
9−10	24,543	−2.9	−3		
11−10	24,740	−2.0	−2		
13−10	24,933	−1.1	−1		
14−10 ?	25,029	−0.7	0		
19−10	25,499	1.1	1		
20−10	25,590	1.5	2		
0−11	23,458	−7.9	−9		
1−11 ?	23,563	−7.4	−6		
2−11	23,672	−6.9	−6		
4−11 ?	23,884	−5.9	−8		
6−11	24,089	−4.9	−3		
7−11	24,192	−4.5	−4		
9−11	24,395	−3.6	−4		
10−11	24,494	−3.2	−4		
12−11	24,691	−2.7	−2		
13−11	24,788	−2.1	−1		
14−11	24,884	−1.5	0		
15−11 ?	24,982	−1.1	−1		
17−11	25,167	−0.3	1		
18−11 ?	25,262	+0.1	+2		
0−12	23,309	−8.6	−8		
1−12	23,418	−8.1	−8		
2−12	23,525	−7.6	−7		
3−12	23,631	−7.1	−8		
4−12	23,736	−6.6			
6−12	23,941	−5.6	−4		
9−12	24,248	−4.2	−5		
10−12	24,348	−3.7	−4		

Appendix F — (Continued)

Band	Frequency in Po_2^{210} (K)	Po_2^{208}-Po_2^{210} Calculated (K)	Po_2^{208}-Po_2^{210} Observed (K)	Po^{208} Po^{209}-Po_2^{210} Calculated (K)	Po^{208} Po^{209}-Po_2^{210} Observed (K)
12–12 ?	24,543	−2.9	−3		
13–12	24,639	−2.5	−3		
14–12	24,734	−2.1	−1		
15–12	24,829	−1.9	0		
16–12	24,925	−1.3	1		
17–12	25,019	−1.0	−1		
20–12	25,295	0.1	0		
0–13 ?	23,163	−9.2	−10		
1–13	23,270	−8.7	−8		
2–13	23,376	−8.2	−8		
3–13 ?	23,483	−7.7	−7		
5–13	23,692	−6.7	−6		
6–13	23,795	−6.2	−5		
8–13 ?	24,001	−5.3	−6		
10–13	24,200	−4.5	−4		
12–13	24,395	−3.7	−4		
13–13 ?	24,494	−3.3	−4		
14–13	24,590	−2.9	−3		
15–13	24,685	−2.4	−2		
19–13	25,058	−0.9	−2		
0–14	23,017	−9.9	−11		
1–14	23,125	−9.4	−10		
2–14 ?	23,233	−8.9	−9		
3–14	23,337	−8.4	−8		
4–14 ?	23,440	−7.9	−6		
5–14	23,546	−7.4	−8		
6–14	23,649	−6.9			
7–14	23,751	−6.4			
10–14	24,055	−5.1	−5		
11–14	24,155	−4.7	−4		
15–14 ?	24,536	−3.1	−2		
16–14 ?	24,630	−2.7	−3		
17–14 ?	24,723	−2.3	−2		
0–15	22,871	−10.5	−10		
1–15	22,980	−10.0	−11		
2–15 ?	23,085	−9.5	−10		
3–15	23,192	−9.0	−10		
4–15 ?	23,295	−8.5	−7		
6–15	23,503	−7.5	−7		
7–15	23,606	−7.0	−6		
9–15	23,810	−6.2	−7		

Appendix F—(Continued)

Band	Frequency in Po_2^{210} (K)	Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
		Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
12–15	24,106	−5.0	−5		
14–15	24,299	−4.1	−5		
15–15	24,395	−3.7	−4		
18–15	24,678	−2.6	−4		
19–15	24,770	−2.2	−2		
1–16	22,875	−10.6	−11		
2–16	22,941	−10.1	−10		
3–16 ?	23,050	−9.6	−9		
4–16	23,152	−9.1	−9		
5–16	23,256	−8.6	−9		
6–16	23,359	−8.2	−8		
8–16 ?	23,563	−7.3	−6		
11–16 ?	23,862	−6.0	−5		
12–16 ?	23,959	−5.6	−8		
13–16 ?	24,055	−5.2	−5		
15–16	24,298	−4.4	−5		
19–16 ?	24,618	−2.9	−4		
20–16	24,706	−2.5			
0–17	22,581	−11.8	−12		
1–17	22,691	−11.3	−12	−8.5	−10
2–17	22,798	−10.8	−12	−8.1	−9
3–17	22,904	−10.3	−12		
4–17	23,008	−9.8	−10		
5–17 ?	23,113	−9.3	−11		
6–17	23,215	−8.8	−8		
7–17	23,318	−8.3	−10		
8–17 ?	23,418	−7.9	−8		
10–17 ?	23,620	−7.0	−7		
13–17	23,914	−5.8	−5		
14–17 ?	24,012	−5.3	−5		
16–17	24,200	−4.5	−4		
18–17 ?	24,387	−3.8	−4		
20–17 ?	24,571	−3.1	−2		
0–18	22,439	−12.4	−12		
1–18	22,548	−11.9	−11		
2–18	22,654	−11.4	−11	−8.6	−9
3–18	22,761	−10.9	−12		
5–18	22,968	−9.9	−9		
6–18 ?	23,075	−9.4	−9		
7–18	23,174	−8.9	−9		
9–18	23,376	−8.1	−8		
11–18 ?	23,572	−7.2	−4		

Appendix F—(Continued)

Band	Frequency in Po_2^{210} (K)	Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
		Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
12–18	23,672	−6.8	−6		
0–19 ?	22,293	−13.0	−14		
1–19 ?	22,403	−12.5	−12		
2–19	22,512	−12.0	−13	−9.0	−10
3–19	22,618	−11.5	−13	−8.6	−10
5–19	22,826	−10.5	−12		
6–19	22,929	−10.0	−9		
7–19	23,031	−9.5	−10		
9–19	23,233	−8.7	−9		
11–19	23,431	−7.8	−6		
13–19 ?	23,623	−7.0			
16–19	23,914	−5.8	−5		
19–19	24,192	−4.7	−4		
20–19	24,283	−4.3	−3		
1–20	22,263	−13.6			
2–20	22,370	−13.0	−12		
3–20	22,476	−12.3	−13	−9.2	−10
4–20	22,581	−11.6	−12		
6–20	22,289	−10.7	−13		
8–20	22,992	−9.8	−11		
10–20	23,192	−8.9	−10		
12–20	23,390	−8.1			
13–20 ?	23,490	−7.6	−6		
0–21 ?	22,008	−14.2	−12		
2–21 ?	22,227	−13.2	−12		
3–21	22,335	−12.7	−13	−9.5	−11
4–21	22,439	−12.2	−12		
6–21	22,646	−11.3	−12		
7–21	22,769	−10.8	−12		
8–21	22,850	−10.6	−11	−7.8	−9
9–21	22,951	−9.9			
10–21	23,050	−9.5	−9		
12–21	23,247	−8.6	−9		
14–21	23,440	−7.8	−6		
15–21 ?	23,537	−7.4	−7		
16–21	23,631	−7.1	−8		
18–21 ?	23,810	−6.3	−7		
19–21 ?	23,904	−5.9	−6		
2–22	22,089	−13.8	−14	−10.4	−11
3–22	22,195	−13.3	−14	−10.0	−12
4–22	22,299	−12.8	−13	−9.6	−10
5–22	22,403	−12.3	−12		

Appendix F — (Continued)

		Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
6−22	22,507	−11.8			
7−22	22,609	−11.4	−12		
9−22	22,811	−10.6	−11		
11−22 ?	23,008	−9.7	−10		
13−22	23,204	−8.9	−9		
16−22	23,490	−7.7	−6		
2−23 ?	21,947	−14.4	−15		
3−23	22,054	−13.9	−14	−10.4	−11
4−23 ?	22,160	−13.5	−14	−10.1	−11
5−23	22,263	−13.0			
7−23	22,469	−12.1	−13		
8−23	22,570	−11.6	−11		
9−23	22,671	−11.2	−11	−8.4	−8
10−23	22,771	−10.7	−12		
11−23	22,871	−10.2	−10		
12−23 ?	22,968	−9.8	−9		
13−23	23,065	−9.4	−10		
14−23 ?	23,163	−9.0	−10		
18−23 ?	23,537	−7.5	−7		
19−23	23,631	−7.1	−8		
1−24 ?	21,706	−15.5	−14		
2−24 ?	21,812	−15.0			
3−24	21,916	−14.5	−14	−10.9	−10
4−24	22,020	−14.0	−15	−10.5	−12
5−24	22,124	−13.5	−13	−10.1	−9
6−24	22,227	−13.0	−12		
8−24 ?	22,429	−12.0	−10		
10−24	22,632	−11.2	−9		
12−24	22,830	−10.4	−12		
13−24	22,929	−10.0	−9		
0−25 ?	21,455	−16.6	−16		
3−25 ?	21,776	−15.1			
4−25	21,882	−14.6	−15	−11.0	−12
5−25	21,986	−14.1	−15	−10.6	−11
6−25	22,089	−13.6	−14	−10.2	−11
8−25	22,293	−12.7	−14		
9−25	22,394	−12.2	−13		
10−25	22,495	−11.8	−12		
11−25	22,593	−11.4	−12		
12−25	22,691	−11.0	−12		
13−25	22,789	−10.6	−13		
14−25 ?	22,884	−10.2	−11		

Appendix F—(Continued)

Band	Frequency in Po$_2^{210}$ (K)	Po$_2^{208}$-Po$_2^{210}$ Calculated (K)	Po$_2^{208}$-Po$_2^{210}$ Observed (K)	Po^{208} Po^{209}-Po$_2^{210}$ Calculated (K)	Po^{208} Po^{209}-Po$_2^{210}$ Observed (K)
15–25	22,980	−9.8	−11		
16–25	23,075	−9.4	−9		
4–26	21,743	−15.1	−16		
5–26	21,848	−14.6	−15		
6–26	21,951	−14.2	−14	−10.7	−10
7–26	22,054	−13.7	−14	−10.3	−11
9–26	22,256	−12.8	−12		
11–26	22,455	−12.0	−13		
13–26	22,650	−11.2	−12		
15–26	22,842	−10.3	−12		
19–26	23,215	−8.8	−8		
1–27 ?	21,292	−17.2	−15		
5–27	21,712	−15.2	−16		
6–27	21,814	−14.8	−15	−11.1	−11
7–27	21,916	−14.4	−14	−10.8	−10
8–27 ?	22,020	−14.0	−15	−10.5	−12
9–27	22,119	−13.6	−14		
10–27	22,219	−13.2	−13		
12–27	22,416	−12.1	−13		
13–27 ?	22,512	−11.7	−13	−9.0	−10
14–27	22,609	−11.3	−12		
16–27	22,798	−10.5	−12	−7.9	−9
19–27 ?	23,075	−9.4	−9		
20–27 ?	23,163	−9.0	−10		
3–28	21,364	−16.7			
4–28	21,470	−16.2	−16		
5–28	21,575	−15.7	−16		
6–28	21,678	−15.2	−15	−11.4	−11
7–28	21,780	−14.8	−14	−11.1	−10
8–28	21,882	−14.4	−15	−10.8	−12
10–28	22,083	−13.5	−14		
12–28	22,279	−12.6	−13		
14–28	22,473	−11.8			
15–28 ?	22,570	−11.4	−11		
16–28	22,664	−11.0	−12		
19–28 ?	22,941	−10.0	−10		
20–28	23,031	−9.6	−10		
6–29 ?	21,545	−15.8	−16	−11.9	−11
7–29	21,646	−15.3	−16	−11.5	−13
8–29	21,747	−14.8	−15	−11.1	−12
9–29	21,848	−14.4	−15		

Appendix F—(Continued)

		Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
10−29	21,947	−14.0	−15		
11−29	22,046	−13.6	−14		
13−29	22,241	−12.8	−13		
3−30 ?	21,096	−17.8	−17		
5−30	21,307	−16.8	−17		
6−30 ?	21,410	−16.4			
7−30	21,511	−15.9	−17		
8−30	21,612	−15.5	−16	−11.6	−12
9−30	21,712	−15.0	−16		
10−30	21,812	−14.5			
11−30	21,911	−14.1	−14		
12−30	22,008	−13.7	−12		
13−30	22,106	−13.3	−14		
14−30	22,202	−12.8			
15−30 ?	22,299	−12.4	−13	−9.3	−10
16−30	22,394	−12.0	−13		
17−30	22,487	−11.6	−12		
18−30 ?	22,581	−11.2	−12		
19−30	22,671	−10.8	−11	−8.1	−8
20−30	22,761	−10.4	−12		
1−31 ?	20,750	−19.4			
7−31	21,377	−16.6	−18		
8−31	21,478	−16.1	−16	−12.1	−12
9−31	21,579	−15.7	−16	−11.8	−12
10−31	21,678	−15.2	−15	−11.4	−11
11−31	21,776	−14.7			
12−31	21,875	−14.3	−14	−10.7	−11
14−31	22,069	−13.5	−14		
18−31 ?	22,444	−11.9			
6−32	21,145	−17.4	−17		
8−32	21,346	−16.5	−18		
9−32	21,445	−16.1	−16	−12.1	−12
10−32	21,545	−15.6	−16	−11.7	−11
11−32 ?	21,646	−15.2	−16	−11.4	−13
12−32	21,743	−14.8	−16		
13−32 ?	21,839	−14.4	−15		
14−32	21,936	−14.0			
15−32 ?	22,030	−13.6	−14		
16−32 ?	22,124	−13.2	−13	−9.9	−9
17−32	22,219	−12.8	−13		
18−32	22,312	−12.4			

Appendix F — (Continued)

Band	Frequency in Po$_2^{210}$ (K)	Po$_2^{208}$-Po$_2^{210}$ Calculated (K)	Po$_2^{208}$-Po$_2^{210}$ Observed (K)	Po^{208} Po^{209}-Po$_2^{210}$ Calculated (K)	Po^{208} Po^{209}-Po$_2^{210}$ Observed (K)
19-32	22,403	-12.0	-12		
0-33 ?	20,372	-20.9	-20	-15.7	-15
4-33 ?	20,799	-18.9	-18	-14.2	-13
7-33	21,110	-17.5	-17		
8-33	21,212	-17.0	-17		
9-33	21,312	-16.6	-16	-12.5	-12
10-33	21,413	-16.2	-17	-12.2	-13
11-33	21,511	-15.7	-17		
13-33	21,706	-14.9	-14		
15-33 ?	21,899	-14.1	-15		
19-33	22.270	-12.6			
3-34 ?	20,563	-19.9			
9-34	21,181	-17.1	-18		
10-34	21,281	-16.7	-17	-12.5	-13
11-34	21,380	-16.3	-17	-12.2	-13
12-34	21,478	-15.8	-16	-11.9	-12
13-34	21,575	-15.4	-16		
14-34	21,672	-15.0	-16		
16-34 ?	21,860	-14.2	-15		
18-34 ?	22,046	-13.5	-14		
6-35 ?	20,750	-19.0			
8-35 ?	20,952	-18.0	-17		
9-35	21,050	-17.6	-18		
10-35	21,149	-17.2	-17	-12.9	-11
11-35	21,249	-16.7	-17	-12.5	-13
12-35 ?	21,346	-16.3	-18		
13-35	21,445	-15.9	-16	-12.2	-12
14-35	21,542	-15.5			
16-35 ?	21,730	-14.8	-15		
17-35	21,825	-14.4			
18-35 ?	21,916	-14.1	-14	-10.6	-10
9-36	20,919	-18.1	-18		
10-36	21,019	-17.7	-17		
11-36	21,118	-17.2	-17	-12.9	-13
12-36	21,216	-16.8	-17	-12.6	-13
13-36 ?	21,312	-16.4	-16	-12.3	-12
14-36	21,410	-16.0			
15-36	21,505	-15.6	-16		
17-36	21,693	-14.8	-15		
4-37 ?	20,279	-20.9	-20		
6-37 ?	20,489	-20.0	-19		

Appendix F — (Continued)

		Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
10–37	20,890	−18.1	−19		
11–37	20,988	−17.7	−17		
12–37	21,086	−17.3	−17	−13.0	−13
13–37	21,184	−16.9	−17		
14–37	21,281	−16.5	−17	−12.4	−13
15–37	21,377	−16.1	−18		
16–37	21,470	−15.8	−16		
17–37 ?	21,561	−15.4			
18–37 ?	21,657	−15.0	−16		
19–37 ?	21,747	−14.6	−15	−11.0	−12
2–38 ?	19,929	−22.4			
7–38 ?	20,460	−20.1	−20		
8–38 ?	20,563	−19.6			
11–38	20,860	−18.2	−14		
12–38	20,958	−17.8	−18	−13.4	−13
13–38	21,055	−17.4	−18	−13.1	−14
15–38	21,249	−16.6	−17	−12.5	−13
16–38	21,341	−16.2	−16		
18–38 ?	21,527	−15.4	−18		
11–39	20,731	−18.7	−16		
12–39	20,829	−18.3	−18		
13–39	20,926	−17.9	−17	−13.4	−13
14–39	21,023	−17.5	−18	−13.1	−13
15–39 ?	21,118	−17.1	−17	−12.8	−13
16–39	21,212	−16.7	−17		
5–40 ?	19,999	−21.9			
12–40	20,702	−18.7	−19		
13–40	20,799	−18.3	−18	−13.7	−13
14–40	20,896	−17.9	−18	−13.4	−13
17–40 ?	21,181	−16.8	−18		
5–41 ?	19,873	−22.3			
12–41	20,576	−19.2	−19		
13–41	20,672	−18.8	−18		
14–41	20,769	−18.4	−19	−13.8	−15
15–41	20,864	−18.0	−18	−13.5	−13
16–41	20,958	−17.6	−18	−13.2	−13
18–41	21,145	−16.8	−17		
20–41 ?	21,329	−16.0	−18		
13–42	20,546	−19.0	−18		
14–42	20,643	−18.6	−19	−14.0	−15
15–42	20,739	−18.2	−19	−13.7	−15

Appendix F—(Continued)

		Po^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
16−42	20,833	−17.8			
17−42	20,926	−17.4	−17	−13.1	−13
18−42	21,019	−17.0	−17		
19−42	21,110	−16.7	−17		
5−43 ?	19,621	−23.2			
10−43 ?	20,131	−21.0	−20	−15.8	−14
14−43	20,518	−19.3			
15−43	20,614	−18.9	−19	−14.2	−14
16−43	20,708	−18.5	−18	−13.9	−14
19−43	20,986	−17.4			
14−44 ?	20,395	−19.7	−19		
15−44 ?	20,489	−19.3	−19		
16−44	20,584	−18.9	−20	−14.2	−15
17−44	20,677	−18.5	−19	−13.9	−14
18−44	20,769	−18.1	−19	−13.6	−15
19−44	20,860	−17.8	−14		
20−44	20,952	−17.5	−17		
15−45	20,366	−19.8	−20		
16−45	20,460	−19.4	−20		
17−45	20,553	−19.0	−19		
19−45 ?	20,739	−18.2	−19	−13.7	−15
20−45 ?	20,829	−17.9	−18	−13.4	−14
12−46 ?	19,957	−21.4			
16−46	20,337	−19.9	−20		
17−46	20,430	−19.5	−19	−14.6	−14
18−46 ?	20,524	−19.1			
19−46	20,614	−18.7	−19	−14.0	−14
13−47 ?	19,929	−21.4			
17−47	20,309	−19.8	−21		
19−47	20,493	−19.0	−19		
20−47	20,584	−18.7	−20	−14.0	−15
17−48	20,187	−20.3	−19		
18−48	20,279	−19.9	−20		
19−48 ?	20,372	−19.5	−20	−14.6	−15
18−49	20,159	−20.3	−20		
19−49	20,251	−20.0	−20	−15.0	−15
20−49	20,343	−19.6	−21	−14.7	−17
19−50	20,131	−20.3	−20	−15.2	−14
20−50	20,223	−20.0	−20		

Appendix F—(Continued)

		Po_2^{208}-Po_2^{210}		Po^{208} Po^{209}-Po_2^{210}	
Band	Frequency in Po_2^{210} (K)	Calculated (K)	Observed (K)	Calculated (K)	Observed (K)
21−51	20,193	−20.0	−20	−15.0	−15
20−52	19,985	−20.7			
21−52	20,074	−20.4	−21	−15.3	−16
21−53	19,957	−20.8			
22−53	20,046	−20.4	−22	−15.3	−17
21−54	19,841	−21.2			
22−54	19,929	−20.8			
23−54	20,017	−20.5	−21		
22−55	19,815	−21.2			
23−55	19,902	−20.8			
23−56	19,787	−21.2			
24−56	19,873	−20.9			
25−58	19,733	−21.3			
25−59	19,621	−21.6			
26−60	19,594	−21.5			
26−61	19,483	−21.6			
27−61	19,566	−21.3			

INDEX

245