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MOUND LABORATORY PROGRESS REPORT FOR MAY, 1965

J. F. Eichelberger, G. R. Grove and L. V. Jones

AEC Research and Development REPORT

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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J. F. Eichelberger
G. R. Grove
L. V. Jones

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The Mound Laboratory Progress Report, issued monthly, is intended to be a means of reporting items of current technical interest in research and development programs. To issue this report as soon as possible after the end of the month, editorial work is limited; and since this is an informal progress report, the results and data presented are preliminary and subject to change.

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SUMMARY

RADIOELEMENTS

Francium-223 Decay The radiochemistry and counting techniques were modified to improve the separation of francium-223 and to measure the half-life. An excellent half-life value for francium-223 of 22.02 ± 0.02 minutes was determined.

Polonium-209 Decay Several counting systems are being evaluated for the detection of the 2.3-kev level in lead-205 which is populated in alpha decay of polonium-209. The half-life of the 2.3 kev level is estimated to be about 37 seconds, but preliminary experiments indicate that the half-life is less than ten seconds.

Polonium-210 in Process Solutions A rapid and accurate method for estimating the polonium-210 content of process solutions was developed. The analytical method involves the sorption of polonium-210 on an anion-exchange resin, followed by gamma counting after elution of interfering radioisotopes.

Actinium-227 Recovery An actinium-227 sample is being prepared by cation exchange technique. Traces of actinium-227 are being recovered from process wastes.

Preparation of Sources for Alpha Spectrometry A simple method was developed for the preparation of alpha sources to be analyzed by an alpha spectrometer equipped with a semi-conductor detector. The procedure consists of evaporating to dryness an aqueous solution of the alpha-emitter, redissolving the residue *in situ* with 0.1 N HNO₃, precipitating with 3 N NH₄OH and drying. The residual NH₄NO₃ is redissolved in 3 N NH₄OH, dried again, and sublimed at a higher temperature. The deposit is washed with distilled water, after which the plate is dried and ignited at red heat. Dramatic improvement is illustrated with several alpha emitters of different chemical properties, including polonium-208 and -209, thorium-230, protactinium-231, uranium-232 and -234, and plutonium-238 and -239.

By providing better distribution of the alpha-emitting nuclides and by removing alpha-absorbing impurities, the same procedure significantly increases the gross alpha counting rate and is recommended for use in improving the accuracy and reproducibility of routine alpha counting.

ISOTOPE SEPARATION AND PURIFICATION

Carbon Isotope Separation

Thermal Diffusion Significant improvement in performance of the 12-column, 8-stage methane thermal diffusion column cascade was observed when the time cycle for interstage gas transport was modified. The modification consisted of the addition of a 15-minute pause between each of the swing cycles.

Chemical Exchange The effect of varying the amine flow rate on the overall separation was studied in three reaction runs carried out on the chemical exchange system. The trend shows the separation decreases with increasing amine flow rates.

Gas Chromatography Additional experiments on temperature control in the 110°K range were carried out. It appears that forced convection of air over a coil cooled by liquid nitrogen will be satisfactory for the planned experiments on isotope separation by gas chromatography.

Analytical The carbon-13 abundance in enriched methane was determined quantitatively from the NMR spectrum of the liquified gas.

Argon Interstage piping was revised to reduce the dead volume. A faster system response is expected.

Krypton Krypton-86 enriched above 49 percent is being accumulated from the second pass for enrichment of krypton-84 and krypton-86. Natural abundance of krypton-86 is 17.4 percent.

Xenon

Thermal Diffusion The six stage cascaded system with the modified Trennschaukel gas circulating system enriched xenon-131 to 16.7 percent after six days.

Gas Chromatography A Linde 4A molecular sieve column was used for further study of xenon-krypton separation. Experiments with helium as a carrier gas gave poor results as did earlier experiments with nitrogen.

Oxygen Oxygen, depleted in oxygen-17 and oxygen-18 by a thermal diffusion column, was further processed to yield a fraction containing less than 0.005 percent oxygen-18 and a fraction containing 0.027 percent oxygen-18. Six 500-milliliter samples of natural and depleted oxygen were prepared for making plutonium-238 dioxide for α, η studies.

Thermal Diffusion Research

Transport Coefficients Additional static separation measurements for neon-20/neon-22 in the six-foot experimental column were made at a hot-wire temperature of 600°C. Good agreement was found between the experimental results and theoretical predictions. Flow measurements for neon isotopes in two of the 12-foot columns gave scattered results. Numerical analysis of the data gave transport coefficients in reasonable agreement with theory for one column; however, because of the scatter, the results are unreliable.

Molecular Beam Scattering The latest experimental runs have yielded the most promising data to date regarding a detection system for neutral particles at thermal energies. Evaluation of these data has permitted valid predictions pertaining to the detection capabilities in a large scale beam apparatus. Various ranges in beam length, source pressure and residual chamber pressure are included.

Collision Integrals The method of integration (Simpson's Rule) which has previously been used to calculate collision integrals is being changed to Gaussian quadrature to minimize troublesome numerical difficulties. In addition, the reprogramming is being done in a series of interconnecting subprograms since it has been found that intermediate data, such as angles of deflection and scattering cross sections, can be used for other projects.

Helium Vapor Pressure Thermometry Thermomolecular pressure data were obtained for helium and air mixtures with a cold temperature of 77°K. The data are compared with data for pure helium-3 and helium-4. The differential equation describing the thermomolecular pressure difference effect, based on the model of Hettner and Weber, is solved for a gas consisting of rigid spheres.

ANALYTICAL

Neutron Activation Analysis of Boron A nondestructive, semiquantitative determination of the impurities in zone-refined boron was made using fast neutron activation analysis. Silicon was readily detectable with

a minimum sensitivity calculated to be about 200 ppm on a five-gram sample. The only other impurity found was the high level of nitrogen ($\sim 0.5\%$).

Coulometric Determination of Uranium-Iron-Nickel Solutions A procedure has been developed for the determination of uranium and iron in solutions containing nickel. A series of 12 determinations for uranium and for iron were made on a standard uranium-iron-nickel solution. The average deviation for uranium was ± 0.2 percent, and for iron ± 0.3 percent, with a relative accuracy for both constituents of greater than 0.2 percent.

RADIOELEMENTS

Basic and applied research is being conducted on a number of radioelements to determine their physical properties, to develop analytical techniques, and to study the basic radiochemistry involved. Of particular interest are alpha emitters, their decay chains, their isotopes, and their chemical homologs.

FRANCIUM-223 DECAY

The chemical separation of francium-223 from other members of the actinium-227 decay chain has been improved by eluting the francium from actinium-227, sorbed on Dowex-50, with 0.5 M HClO₄, rather than with 1.0 M HClO₄, as previously reported (MLM-1250, p. 18). It has been found that increasing amounts of thallium-207 are eluted with the francium-223 after the column has been milked several times for francium-223. The use of the more dilute HClO₄ allows more separations before thallium-207 starts to elute.

The thallium-207 contamination was discovered when several changes were made in the method of accumulating half-life data. Previously, the gamma rays detected in a well crystal were accumulated in a multi-channel analyzer (MCA), operating in the multiscaler mode. The detector output was fed directly to the MCA and was processed by the built-in amplifier and analog-to-digital converter (ADC). Because the ADC circuit will not accept data during the time that any one pulse is being processed, some of the detector pulses arriving at the ADC are rejected, and are not accumulated in the MCA memory. The external timing device, which provides channel advance signals to the MCA, operates independently of the ADC circuit, with the result that fewer counts are accumulated in the analyzer memory than are detected in the NaI(Tl) crystal. Since more counts are undetected at high counting rates, the first several channels are most affected. The counting system was modified by employing an external amplifier discriminator so that the MCA amplifier and ADC circuits were not used. The output of the external amplifier was routed directly to the MCA memory. The first half-life determination with the modified counting system showed the presence of a 4.8-minute activity, which agreed well with the half-life of thallium-207. After the thallium-207 had been identified, the concentration of the HClO₄ was lowered, as explained above.

Several half-life determinations were made using the improved separation and counting techniques. A least-squares fit of the data for one run, counted for four half-lives, gave a half-life of 22.02 minutes, with an internal probable error of ± 0.02 minute. There was no indication of a short-lived activity.

Gamma-ray counting results in a much better value for the half-life than beta counting. The growth of daughter activities in the francium-223 causes more interference in beta counting, since the francium-223 daughters, after radium-223, are mostly short-lived alpha emitters, which would be counted in a beta proportional counter. The gamma rays of the daughter nuclides are about an order of magnitude less abundant.

Several gamma-ray coincidence experiments were made on francium-223 before the thallium-207 contamination was found. These experiments are being repeated in order to determine the effect of the thallium-207 bremsstrahlung.

POLONIUM-209 DECAY

A level at 2.3 kev in lead-205 should be populated in the alpha decay of polonium-209. A partial level scheme¹ for lead-205 is shown in Figure 1. There are several reasons for believing that the spin assignments of Vegors, et al. for the ground state and 2.3 kev level are incorrect, and that the ground state spin

¹S. H. Vegors, Jr., R. L. Heath, and D. G. Proctor, Nucl. Phys., 48, 230 (1964).

is $1/2$, while the 2.3 kev level is $5/2$. Alpha decay of polonium-209 (ground state = $1/2^-$) can populate the 2.3 kev level in either case; however, the amount of feeding to the 2.3 kev state is strongly dependent on the spin assignment.

If the spin assignments of Figure 1 are correct, the main alpha group of polonium-209 (99.44%) will feed the 2.3 kev level.² But if the lead-205 ground state is $1/2^-$, the 2.3 kev state can only be populated by the weak (0.56%) alpha decay to the 262.9 kev level,² which then decays (about 70%) by gamma-ray emission to the 2.3 kev state.¹

Figure 1. Partial Level Scheme for Pb^{205} .

The half-life of the 2.3 kev level can be estimated from the half-life of other E2 transitions in the lead region. The most comparable E2 gamma transition occurs in lead-203, where the 126 kev level decays with a half-life of 7.5×10^{-10} seconds.³ Since the lifetime for E2 transitions is inversely proportional to the fifth power of the decay energy,⁴ the lifetime of the 2.3 kev state is expected to be about 37 seconds.

Several counting systems were investigated for the detection of the 2.3 kev gamma ray. The 2.3 kev photons are difficult to detect because of their high absorption. The half thickness for 2.3 kev gamma rays in aluminum is only about 0.5 mg/cm^2 (0.0000728 inch). A thin NaI(Tl) crystal mounted on a multiplier phototube was not satisfactory because of phototube "shot" noise peaks (after amplification) in the energy region of interest.

The lead fraction was separated by elution from an anion exchange resin on which a mixture of polonium-208 and polonium-209 was sorbed. The fraction was counted by liquid scintillation techniques. The liquid scintillation counting system was operated with the same settings used for tritium beta counting, and no activity was observed. Further work with the liquid scintillation counter would be desirable. A small amount of iron-55, which decays by electron capture to manganese-55 with the emission of an x-ray of 5.9 kev, has been ordered, so that instrument settings can be adjusted to give maximum efficiency for low-energy photons.

A gas-flow proportional counter which had been used for low-geometry alpha counting was modified by replacing the sample holder slide with a window of aluminized Mylar,[®] which has a surface density of about 0.5 mg/cm^2 . The modified detector, with flowing P-10 gas, has been used to detect photons with as little as 5.41 kev energy (from electron-capture decay of manganese-54). The resolution is of the order of 25% (full width at half maximum); the spread is due mostly to the detector itself. The detector response is not linear in the energy region below about 6 kev, and it is not certain that the counting system will detect gamma rays of 2.3 kev energy.

Several experiments were made with the proportional counter. The lead-205 was separated from polonium-209 sorbed on an anion-exchange resin by elution with concentrated HCl, which was then evaporated to dryness on a silver foil. The time from the start of separation to the start of counting was about one minute. No low-energy gamma-ray events were detected. Assuming that the counting system is capable of detecting 2.3 kev

²G. R. Hagee, R. C. Lange, and J. T. McCarthy, *Bull. Am. Phys. Soc. Ser II*, 9, 19 (1964).

³I. Bergstrom, C. J. Herrlander, P. Thieberger, and J. Uhler, *Arkiv Fysik*, 20, 93 (1961).

⁴G. Friedlander, J. M. Kennedy, and J. M. Miller, *Nuclear and Radiochemistry*, John Wiley & Sons, Inc., New York, (1964) p. 258.

photons, and that as few as 20 disintegrations per minute could be detected, an upper limit for the half-life of the 2.3 kev level in lead-205 can be set at less than ten seconds, depending on the spin of the level.

Another proportional counter is being constructed in which the outside wall is graphite impregnated phenolic resin. This type of counter is reported to give better resolution, and the use of the plastic wall avoids the copper and zinc x-rays which may be excited in a brass-wall counter.

POLONIUM-210 IN PROCESS SOLUTIONS

The polonium-210 content of HCl solutions, containing reactor-irradiated bismuth after it has passed through a bismuth metal scrub bed, can be estimated by gamma-ray methods. The polonium deposits on the bismuth metal, and assay of the polonium content of the scrubbed solution is required to determine whether the solution must be rescrubbed. A rapid analysis is desirable since the scrubbed solution must be held until the polonium-210 content is known.

The analytical method involves sorption of polonium 210 on an anion-exchange resin from concentrated HCl, and gamma counting the solution after interfering radioisotopes are removed. Radioisotopes which interfere with gamma-ray counting of polonium-210, such as iron-59, cobalt-60, and silver-110m, can be eluted from the resin with various concentrations of HCl.

Five determinations of a scrubbed solution gave a polonium-210 content equivalent to 0.75 ± 0.15 curie in 50 liters. This result compares favorably with the results of direct alpha counting (0.585 ± 0.015 curie/50 liters), but is much lower than the result obtained by serial dilution in the process area (2 curies/50 liters). The accuracy of the gamma-counting method would be greater at higher polonium-210 concentrations.

ACTINIUM-227 RECOVERY

The ion exchange column described previously,⁵ a 30 cm column loaded with Dowex[®] resin (AG 50W-X8, 50-100 mesh), was tested by preferentially eluting nonradioactive elements and iron at 60° and 70°C. A metering pump was used to feed the elutrient through the resin at a rate of 0.7 to 1 ml/minute. Essentially all iron was eluted by 75 ml of 2 M HCl. Barium and lanthanum, nonradioactive substitutes for radium and actinium, respectively, behaved in accordance with previous experiments.

The separation and purification of actinium-227 by cation exchange techniques has nearly been completed. Recovery of residual actinium from solid scrap and waste solutions is now underway. Solutions which were checked through the collimator tube by the gamma multichannel analyzer and found to contain actinium-227 were combined and evaporated to a low volume. Used beakers and other glassware were rinsed with warm 4 M HCl and the solutions checked by the multichannel analyzer. Those solutions found to contain actinium-227 were combined and evaporated to a small volume in anticipation of a recovery run.

PREPARATION OF SOURCES FOR ALPHA SPECTROMETRY

The two principal requirements to be considered in preparing sources for alpha spectrometry are: (1) that the material be deposited in a small area; and (2) that the deposit be as thin as possible. The first requirement can be simulated by low geometry counting or by collimation; both of these methods are easily applied and widely used, although they have the effect of severely limiting the effective counting rate.

⁵See MLM-1254

The second requirement cannot be so easily circumvented, and the techniques for achieving sample thinness vary in complexity according to the chemical nature of the element under study. The methods used range from the spontaneous electrodeposition of polonium on silver or copper foil⁶ to the distillation of radium at elevated temperatures.⁷ Specific methods for individual radioisotopes have been summarized in a number of publications.^{8,9,10}

The requirements for quantitative alpha counting are similar, although not quite as stringent as those for alpha spectrometry. However, any chemical or physical operation performed on a mixture of non-isotopic nuclides may cause their partitioning and yield a source which is not representative of the material being analyzed. From the standpoint of analytical radiochemistry, therefore, it is desirable to have a procedure which precludes such fractionation without significantly sacrificing the degree of energy resolution obtainable by other methods.

Reagents and Equipment

HNO₃ - 0.1 N and 1 N

NH₄OH - 3 N

Alcoholic KOH - 125 g. KOH dissolved in 125 ml. H₂O, cooled to room temperature and diluted to one liter with 95% ethanol.

Tempilstik[®] or Tempilaq[®] melting point compounds (Tempil Corp., 132 W. 22 Street, New York, New York).

Krylon[®] Crystal Clear Spray Coating No. 1300A (Krylon Corp., Norristown, Pa.).

Two thermostatically controlled hot plates.

A short length of round brass rod, 1/4 - 1/2 inch diameter, ground flat on one end. (A glass vial of the same diameter will serve as well.).

Alpha spectrometer system. The spectra shown here were made with a Nuclear Diodes Model SL 1-20-10 S-type silicon barrier detector having an active area 10 mm. in diameter. The remainder of the system consisted of a vacuum chamber (Instrument and Development Products Model C-202), a low-noise preamplifier and amplifier (Oak Ridge Technical Enterprises Models 101 and 201), and a 400-channel analyzer (Radiation Instrument Development Laboratory Model 34-12).

Alpha scintillation counter (Eberline Instrument Corp. Model SAC-1).

Recommended Procedure The backing plate, whether of platinum, stainless steel, glass or other material, must be flat, smooth and clean. (For the examples shown below, all samples were mounted on platinum foil). The plate is cleaned by agitation for a few minutes in alcoholic KOH, then rinsed thoroughly with water and dried with absorbent paper. The brass rod is set upright in the center of the plate. The plate is sprayed with Krylon methacrylate coating, and the masking rod is removed.

The plate is transferred to a thermostatically controlled hot plate set at 90-100°C. (Tempilaq melting point compounds are convenient for determining the surface temperature, but precise measurement is not necessary; the proper temperature may be approximated by setting the hot plate so that 4-5 minutes are required to evaporate 0.1 ml. of water from the 1/4-inch diameter metal surface. A 1/2-inch diameter surface will require 0.25 ml. of water to cover and approximately seven minutes to dry.)

⁶I. Feldman and M. Frisch, *Anal. Chem.*, **28**, 2024 (1956).

⁷F. Asaro, F. Stephens, Jr., and I. Perlman, U. S. At. Energy Comm. Rpt. UCRL-2244 (June 1953).

⁸D. L. Hufford and B. F. Scott, National Nuclear Energy Ser. IV-14B, p. 1149, McGraw-Hill Book Co., Inc., New York, (1949).

⁹J. E. Gindler, "Radiochemistry of Uranium" Natl. Acad. Sci.-Natl. Res. Council Report NAS-NS 3050 (March 1962).

¹⁰G. D. O'Kelley, "Detection and Measurement of Nuclear Radiation" Natl. Acad. Sci.-Natl. Res. Council Report NAS-NS 3105 (April 1962).

After one or two minutes, the uncoated area of the sample plate is covered with 1 N HNO₃ and allowed to stand for two minutes. The plate is removed from the heat and rinsed thoroughly with distilled or demineralized water. The excess water is shaken off, and the plate is dried at 90-100°C.

An aliquot of the radioactive solution is deposited in the uncoated area of the plate and allowed to evaporate to dryness. The residue is covered with two drops of 0.1 N HNO₃ and heated for two minutes. One drop of 3 N NH₄OH is added, and the solution is evaporated to dryness. The plate will usually have a visible residue of NH₄NO₃.

The residue is covered with two or three drops of 3 N NH₄OH and again evaporated to dryness.

The residual NH₄NO₃ is driven off by heating the plate to a higher temperature, preferably on a second hot plate or under an infrared lamp. Precise temperature measurement is unnecessary; the plate is heated until the residue melts and fumes of NH₄NO₃ are given off. However, excessive heat should be avoided, since boiling may result in a loss of material.

This treatment is usually sufficient to yield a satisfactory alpha spectrum, but additional improvement can often be obtained by rinsing the plate in distilled water after it has been allowed to cool to room temperature. (However, washing will partially desorb radium isotopes if they are present, and this step should be omitted if quantitative retention of radium is desirable.)

If polonium is absent, the methyl methacrylate coating is eliminated by igniting the stainless steel or platinum plate at red heat for a few seconds. If long-lived polonium isotopes are present, or if the backing plate is of glass or some other low melting material, the coating may be dissolved away in acetone without significant loss of alpha activity.

Experimental Results The effect of each step in the recommended procedure is illustrated in Figure 2. The source of alpha activity was a 20-microgram sample of uranium-234 mounted in an area 1/2-inch in diameter. The source contained (on a weight basis) a trace of uranium-232,

Each step produced a significant improvement in energy resolution and, except for the washing step, a significant increase in the gross alpha counting rate (Table I). The overall increase in counting rate was 16.4 percent.

Table I
Resolution of Uranium-234 Alpha Spectrum

Figure 2 Spectrum	Treatment	Height (Counts/channel)			Alpha Scintillation (counts/minute)
		4.77 mev peak	4.72 mev peak	Valley	
A	Evaporation from 1 N HNO ₃	570	497	412	62,031
B	NH ₄ NO ₃ sublimation	963	759	604	69,318
C	Washing with H ₂ O	1341	938	736	69,515
D	Ignition	1727	1024	751	72,173

The final step (Figure 2D) yielded a full width at half maximum height (FWHM) of approximately 0.038 mev (0.8%) at the 4.768 mev peak of uranium-234. (By comparison, a nearly "weightless" sample of polonium-208, electrodeposited on silver foil, had a resolution of 0.026 mev, or 0.5% FWHM at 5.108 mev). The two peaks of uranium-232, at 5.261 and 5.318 mev,¹¹ are also well defined.

¹¹D. Strominger, J. M. Hollander, and G. T. Seaborg, *Revs., Mod. Phys.*, 30,585 (1958).

Figure 2. Alpha spectrum of a 20-microgram sample of uranium-234 showing stepwise improvement in energy resolution.

As a general rule, a small quantity of an alpha emitter will have less self-absorption and yield a better spectrum than a larger quantity of the same nuclide. However, chemical impurities frequently contribute more self-absorption than the radioisotope itself.

A four-year old sample of protactinium-231, dissolved in a mixture of 0.002 N HF and 0.001 N H₂SO₄ and stored in a glass container, was the source of the two spectra in Figure 3. Although the source contained only three micrograms of protactinium-231, impurities leached from the glass storage vessel absorbed so much of the alpha radiation that the peaks were diffused almost beyond recognition (Figure 3A). Treatment by the recommended procedure produced a cleaner alpha source, permitting the peaks, not only of protactinium-231, but of its decay products as well, to be resolved (Figure 3B).

The improvement in resolution was even more dramatic when a sample of thorium-230 was prepared. The source contained 7.5 micrograms of total thorium, of which 0.7 micrograms was thorium-230. A simple evaporation from 1 N HNO₃ produced the almost useless spectrum in Figure 4A. The ammonium nitrate treatment alone increased the gross alpha count by 14 percent, with a respectable resolution of 0.047 mev (not shown). After washing and ignition, the resolution at 4.682 mev was 0.034 mev (0.7% FWHM Figure 4B).

Figure 5 illustrates the resolution of two alpha peaks of similar energies belonging to nuclides of significantly different chemical properties. A synthetic mixture of polonium-208/209 and plutonium-238/239 in 1 N HCl was evaporated on a platinum disk and treated by the recommended procedure. Spectrum A was obtained after the initial evaporation and Spectrum B after the methacrylate coating had been dissolved away in acetone. The two major peaks at 5.108 mev (Po²⁰⁸) and 5.147 mev (Pu²³⁹) are clearly identifiable in Spectrum B, and the two minor peaks at 4.877 mev (Po²⁰⁹) and 5.495 (Pu²³⁸) have been significantly improved.

Discussion and Conclusions The recommended procedure is based on techniques developed in the study of residue adsorption^{12,13}, whose basic hypothesis is that adsorption of inorganic cations occurs at the trace level under the same conditions as those which would lead to precipitation or crystallization at the macroscopic level.

Since all alpha emitters, except radium and radon, are isotopes of elements which are precipitable by ammonium hydroxide, a widely applicable adsorption procedure is feasible. The improvement in resolution following the dissolution and reprecipitation of a dried residue reflects a difference in the degree of dispersion between a crystalline salt and a flocculent precipitate. Sublimation of the residual ammonium nitrate is necessary only to eliminate a chemical impurity which would attenuate the alpha radiation.

Washing with water is useful because it can solubilize the most common trace impurities found in reagents stored in glassware (such as sodium and calcium salts). However, to insure that the washing does not also eliminate that part of the adsorbate which is deposited on the soluble impurities, a second evaporation with ammonium hydroxide is carried out before the ammonium nitrate sublimation.

Although radium hydroxide is soluble in water,¹⁴ radium isotopes are fairly well adsorbed under the conditions recommended, probably because of the traces of carbonate usually present in commercial ammonium hydroxide. For this reason, unless quantitative retention of radium is required, the washing step is often beneficial. (See Figure 3, for example).

¹²H. W. Kirby, *J. Inorg. Nucl. Chem.*, **25**, 483 (1963).

¹³H. W. Kirby, *Ibid* (In Press).

¹⁴G. Bouissières, "Radium", *Nouveau Traité de Chimie Minérale*, ed. by P. Pascal, vol. IV, p. 949. Masson et Cie, Paris (1958).

Figure 3. Alpha Spectra of Protactinium-231.

Figure 4. Alpha Spectra of Thorium-230.

Figure 5. Alpha Spectra of a Synthetic Mixture of Plutonium-238/239 and Polonium-208/209.

Dissolution of the methacrylate coating with acetone is substituted for ignition in the special case of polonium sources, because of the well-known volatility of polonium compounds.¹⁵ However, for short-lived polonium isotopes supported by their longer-lived parents (such as Po^{214,215,216}) this modification is unnecessary.

The increase in gross alpha count observed with uranium-234 (Table I) occurs, to some extent, with all radionuclides, but, because of self-absorption, it is most pronounced when microgram amounts of material are being counted. It seems clear, therefore, that this or a similar procedure would be of value in improving the accuracy and reproducibility of routine alpha counting.

Since the recommended procedure is a simple one, requiring little equipment and virtually no experience, it should prove as useful to the non-chemist as to the analytical radiochemist.

¹⁵H.V. Moyer, ed., "Polonium", U.S. At. Energy Comm. Report TID-5221 (July, 1956).

ISOTOPE SEPARATION AND PURIFICATION

Under the sponsorship of the Division of Research, Mound Laboratory is responsible for furnishing material to be used in the physical sciences to further the progress of science and technology in the public interest. After recovery, purification and concentration, research quantities of isotopes are furnished to installations for research programs in the physical sciences. Purified helium-3 and the isotopes of other noble gases and carbon-13 are available for distribution in research quantities. Methods of separation and purification are being studied.

CARBON ISOTOPE SEPARATION

Thermal Diffusion

The methane in the lower sections (toward the product end) of the 12 column - 8 stage thermal diffusion column cascade is circulated between the stages by a modification of the "Gasschaukel" method of Clusius and Buhler.¹⁶ On a timed cycle a small volume of gas is pumped out of the bottom of the last stage (stage 8) into a storage reservoir. A corresponding amount of gas flows from the bottom of stage 7 into the top of stage 8, from the bottom of stage 6 into the top of stage 7, etc. At a later time in the cycle the stored gas is returned to the system (at stage 8) and interstage movement of gas in the opposite direction takes place.

Previously, the cascade was operated with a gas swing cycle of two minutes. Last month, during recovery from a small loss of holdup, the swing cycle was modified:

- (1) a volume of 400 stp cc was pumped out of the system into the reservoir;
- (2) after a 15 minute pause, the stored gas was returned to the system at stage 8, and
- (3) after a second 15 minute period, the cycle was repeated.

The new cycle caused a significant improvement in performance (Figure 6). Within a few days the mass 17 fraction at the product withdrawal point increased from 91 to 95 percent. This increase was not associated with a significant increase of the system holdup of the desired isotope, but is attributed to a more effective distribution of the holdup.

These results show that the performance of the cascade is sensitive to variations in the swing cycle. It is evident, therefore, that the gasschaukel scheme should be used only in those cases for which holdup and reliability are crucial factors.

Chemical Exchange

Several experimental runs on the carbon dioxide-carbamate chemical exchange system were performed to study the effect of flow rates on overall separation. In these initial runs the amine flow rate was varied while carbon dioxide flow rate was held constant. Other reaction conditions were maintained constant throughout the experiments.

A comparison of the results obtained from three experimental runs is shown in Figure 7. In general, as the amine flow rate is increased, the overall separation factor decreases, as expected. But while the trend is definitely indicated in the results, more information is required to develop the correlation between the two variables.

¹⁶K. Clusius and H. Buhler, Z. Naturforsch., 9a, 775 (1954).

Figure 6. Effect of Gasschaukel on Carbon-13 Separation in Methane.

Undecomposed carbamate recycled and remixed in the chemical exchange system. Although the maximum amount of carbon dioxide remaining in the amine solution after decomposition did not exceed 0.20 percent in three runs, it is still high enough to introduce significant lowering of the overall separation factor. This fact reduces the reliability of conclusions drawn from a comparison of the three experimental runs.

Gas Chromatography

A series of experiments are planned to test the feasibility and efficiency of the chromatographic separation of carbon-13 substituted compounds. Initially, an attempt will be made to separate $C^{12}H_4$ and $C^{13}H_4$ chromatographically. Inasmuch as Gant and Yang¹⁷ have already separated CH_4 , CH_3D , CH_2D_2 , CHD_3 , CD_4 , CH_3T , CH_2T_2 , CHT_3 , and CT_4 , an attempt will also be made to check their work.

Since the ratio of the vapor pressure of $C^{13}H_4$ to $C^{12}H_4$ increases as temperature decreases, the most favorable temperatures for chromatographic separation are near the boiling point of methane, 112°K. It is desirable to hold the column temperature variation to within $\pm 1^\circ K$ or less to increase the validity of the collected

Figure 7. Separation as a Function of Amine Flow Rate.

¹⁷P. L. Gant and K. Yang, J. Am. Chem. Soc., 86, 5053-4 (1964).

data, particularly those of the measured retention times.

An investigation was made to see how small the temperature variation could be held. A potentiometric controller with a chromel-alumel thermocouple was used as the temperature detector in the apparatus shown in Figure 8. The controller operated a pair of solenoid valves to transfer the necessary amount of liquid nitrogen by pressurizing or venting the dewar. The arrangement of the brass tube and fan blades was calculated to circulate air through the dewar rapidly, thus reducing the temperature gradient in the controlled volume, and reducing the lag time between temperature changes in the controlled volume and the operation of the cooling coil. The smallest temperature variation obtainable with this arrangement was about $\pm 1.5^\circ\text{K}$. It is likely that with improved insulation, a more sensitive control system, and an improved circulation system, the variations could be reduced to $\pm 1^\circ\text{K}$ or less.

Analytical

The carbon-13 content in methane can be determined nondestructively by nuclear magnetic resonance (NMR). The ratio of carbon-13 and carbon-12 can be measured from the proton NMR spectrum of liquefied methane (Figure 9). Those molecules containing nonmagnetic carbon-12 nuclei give a single proton resonance peak, while those containing the magnetically active carbon-13 nuclei give two well-separated (120 cps) peaks corresponding to the two magnetic energy states of carbon-13.

The methane gas was liquefied in a glass dewar specially constructed to hold a liquid sample in the NMR probe assembly. The gas was liquefied when it came in contact with a finger refrigerated with cold nitrogen gas. At least one liter of gas at 0.5 atmosphere pressure was necessary to obtain a satisfactory spectrum.

The natural abundance of carbon-13 in methane is 1.1 percent, and therefore, its NMR spectrum consists of a single strong central peak with two barely visible peaks on either side due to the methane molecules containing carbon-13 nuclei. In carbon-13 enriched methane, the two outer peaks are more pronounced than the center peak (Figure 10). The abundance of carbon-13 is calculated by dividing the total area of all the proton peaks into the area of the two outer peaks.

ARGON

To improve the performance of the four-stage, argon thermal diffusion column cascade, the gas volume of the interstage circulating lines between stages 2, 3, and 4 was reduced by installing smaller diameter lines. The changes are expected to shorten the time required to reach a substantial peak of argon-38. The basis for these changes is given below.

Figure 11 shows the argon-38 buildup at 12G, the sample port at the middle of the 96-foot long cascade and at 13G, the sample port 24 feet above the middle of the cascade. The third curve represents the average concentration in the third stage between 12G and 13G.

For 180 days the cascade was operated so that the argon-38 peak concentration was maintained at 12G. The concentration at this point reached about 13.0 percent in 110 days where it remained steady. The decrease in transport of argon-38 into the system at that time was attributed to attaining a steady state, in which argon-38 was leaving at the bottom of the cascade at the same rate as it entered the system. The limit of the separating capacity of the bottom half of the cascade had been reached, so that no appreciable quantity of argon-38 was transported into the system by thermal diffusion.

Figure 8. Temperature Controlled Volume with Rapid Air Circulation.

Figure 9. Proton Resonance of Natural Methane. Figure 10. Proton Resonance of C^{13} Enriched Methane.

Figure 11. Performance of the Argon Thermal Diffusion Column Cascade Over a 230-Day Period.

Approximately 600 ml of gas were contained in the circulating lines (3/8-in. diameter) at 12G between stages 2 and 3. This large volume lengthened the time required to reach the peak.

The argon-36 flow was increased after 180 days to move the argon-38 concentration profile peak up toward 13G. Under this condition the decrease of argon-38 in the raffinate stream should cause less argon-38 to be carried out in the waste and increase the transport into the column. Figure 11 shows a negative slope for both the 12G and 13G curves. The slope of the 13G curve should increase, and the 12G curve slope should decrease due to the large dead volume between stages. This probably contributed to the contradiction in performance. This transient unbalance in transport in stages showed up at 183 days where the 13G concentration decreased. When the argon-38 peak shifted upward, the argon-38 concentration increased.

The large dead volume between stages slowed down the operation of the cascade to the point where it took several days to detect a change in column concentration when a product flow rate was changed. The 3/8-inch line was removed between stages 2, 3 and 4 and replaced with 3/16-inch line. The last two points on the average concentration curve at 220 and 230 days show the sharp increase in the average concentration of argon-38 in the third stage.

Additional data will be collected to compare the increase of argon-38 to that in the system with large dead volume.

KRYPTON

A two-column, two-stage thermal diffusion cascade system is being used for the second pass in enriching krypton-84 and krypton-86. With circulation of 30 percent krypton-86 across the top of the cascade, an average product draw-off rate of 12.8 ml per hour from the bottom allowed the product concentration to be maintained above 49 percent krypton-86. Calculations at a flow rate of 20 ml per hour indicated that a product concentration of 46 percent krypton-86 could be expected. The actual lower flow rate allowed separation to the higher concentration. When nine liters of this product are accumulated, the third pass for enrichment to about 70 percent krypton-86 will be started. The natural abundance of krypton-86 is 17.4 percent.

XENON

Thermal Diffusion The eight-column, six-stage thermal diffusion unit with a modified Trennschaukel gas circulating system for interstage transport was converted to enrich xenon-131, the lightest isotope in fission-product xenon. The modification consisted of connecting a 6.5-liter cylinder to the discharge side of the compressor located at the bottom of Column 8 to serve as a feed reservoir, and connecting a 0.5-liter lecture bottle to the suction discharge of the compressor located at the top of the first stage to serve as the product cylinder for the xenon-131.

Prior to starting the swing system the amount of krypton-85 contaminant that would be enriched with the xenon-131 was calculated. The total krypton-85 in the system, and thus, the total amount that could be enriched with the xenon-131, is shown below for the system operating at 170 torr pressure:

Feed Gas Concentration (mole % Kr-85)	Total Activity Present (microcurie)
2×10^{-5}	1828.7
5×10^{-10}	0.046

In order to minimize the number of curies in the product, the gas containing 5×10^{-10} mole percent krypton-85 was used for feed.

The product cylinder at operating pressure contains approximately 90 ml of gas. On each cycle, all 90 ml are drawn into the head of the product compressor which serves as a mixing chamber for the product gas and the gas at the top of stage one.

The variable leak at the feed end was set to provide the same amount of transport as exists at the product end, i.e. approximately 90 ml.

After six days of operation the top of the first stage was enriched to 16.7 percent xenon-131. Six days later the xenon-131 was enriched to 23.9 percent.

Chromatography Xenon obtained as a reactor off-gas contains the radioisotope krypton-85 as an impurity, which can be reduced by chromatography techniques. The efficiency of this purification process is being studied.

The heats of absorption of krypton and xenon are being measured chromatographically. Separations were made with helium carrier gas on 50/60 mesh Linde molecular Sieve 4A (a synthetic zeolite) at 166°K and 210°K. As in the separations with nitrogen carrier gas reported previously (MLM-1250), the retention times were short and close together. With helium, the retention times were approximately 0.3 minute for krypton and approximately 0.6 minute for xenon. As in the separations using a nitrogen carrier gas, the retention times apparently were temperature independent in the range covered. Either the total surface area in the column is too small for the amount of sample used, or the pore size of the absorbent, 4A diameter, limits the amounts of xenon that can enter the absorbent. In either case, this absorbent would not be suitable for application to xenon purification.

In the investigation just completed a double peak was noted for krypton. This was the result of dead space in the sample system that delayed part of the sample. Because the zero time reference gas, nitrogen, was run separately and not with the sample, the nitrogen peak would not mask the xenon peak. As a result, the dead space in the sample system that would have been occupied by the reference gas held up the sample. The system has been modified to eliminate this dead volume.

OXYGEN

The neutron flux from plutonium-238 dioxide by (α , n) reaction with one or both of the heavy stable oxygen isotopes, oxygen-17 and oxygen-18, may be reduced by use of oxygen depleted in oxygen-17 and oxygen-18. (The natural abundances of these isotopes are 0.037 and 0.20% respectively.)

In an earlier experiment (MLM-1250) 10.5 STP liters of depleted oxygen were prepared in a single pass through a 12-foot thermal diffusion column. This sample, containing 0.02 percent oxygen-18 and 0.015 percent oxygen-17, was used as the starting material for a second separation experiment. The 12-foot prototype column was equipped with 1.5-liter reservoirs and circulating pumps at top and bottom (Figure 12). The gas previously prepared was put into the system at a resultant pressure of 2040 torr. (The maximum static separation pressure for this column is 1820 torr.) A small leak from the bottom reservoir reduced the pressure to 1780 torr over a four-day period. After the leak was repaired, the separation experiment continued for an additional 13 days for a total of 17 days.

The top and bottom reservoirs were then closed and removed from the system. Each reservoir contained 3.5 STP liters of gas.

Carbon dioxide samples were prepared by combustion of methane in the oxygen. Mass spectrometric analyses of these samples showed that the top reservoir contained less than 0.005 percent oxygen-18 and that the bottom reservoir contained 0.027 percent oxygen-18.

Figure 12. Oxygen Isotope Separation System.

Figure 13. Separation as a Function of Pressure for $\text{Ne}^{20}\text{-Ne}^{22}$ in Column E5 ($T_h = 600^\circ\text{C}$).

Six 500-ml samples of oxygen were reacted with plutonium-238 hydride to form plutonium dioxide. Two of the oxygen samples were natural oxygen (for use as controls), two were from the top reservoir, one from the bottom reservoir, and one made up to 50% natural oxygen and 50% oxygen from the top reservoir. Analytical and neutron counting results are not yet available on the plutonium dioxide samples.

THERMAL DIFFUSION RESEARCH

Transport Coefficients Static separation measurements for neon in column E5 were repeated* for a wire temperature of 600°C . The first series of measurements, reported in March 1965 (MLM-1250) gave separation factors 15 percent greater than those calculated from theory with Lennard-Jones shape factors. Experimental work on the first series was stopped when vibration of the hot wire was observed. The vibration was dampened by increasing the weight on the hot wire from 1860 to 3600 grams.

The results of the second series of static separation measurements, shown in Figure 13, agree with the theoretical curve. A critical re-examination of the data for the first series revealed an error in the calculation of the experimental hot-wire temperature. Thus, the first measurements were for a wire temperature of 650°C rather than 600°C .

Separation as a function of neon flow in columns E1 and E2 is being measured. A recent set of measurements is shown in Figure 14. The curve shown on the plot was constructed from a numerical analysis of the data. The curve corresponds to a value of $3.56 \times 10^{-4} \text{ g/atm}^2\text{-sec}$ for the column transport coefficient H' . Although this is close to the theoretical value of $3.98 \times 10^{-4} \text{ g/atm}^2\text{-sec}$, the scatter of measured values of $\ln q$ does not engender confidence in the experimental result. The experiments are being extended to other pressures and to lower flow rates at this pressure. The recent improvement of the pressure control system for this column should help in reducing experimental scatter; however, other possible sources of variation are being examined.

Molecular Beam Scattering The latest beam detection method was evaluated using two VIC TV 34 ion gage control units. A collimated beam of argon particles at room temperature was intercepted by a movable slit assembly at the entrance to an ion gage detector

*Columns are defined in report MLM-1245.

operated by a Vacuum Instrument Corporation control unit. Another ion gage was placed in the vacuum chamber, not exposed to the beam, and used as a residual pressure indicator.

Figure 14. Separation as a Function of Flow Rate in Column EI ($T_h = 800^\circ\text{C}$, $p = 300$ torr).

In the three final runs in this series of experiments, source pressures of 10^{-3} , 10^{-2} and 10^{-1} torr were used with corresponding residual pressures of 10^{-6} , 10^{-5} and 10^{-4} torr. A constant slit area of 10^{-2} cm^2 was used. The data obtained in these runs were used to predict the performance of this type of detection system in a molecular beam scattering apparatus operating at lower residual pressures.

In designing the pumping system for the large scattering chamber it is necessary to know the extent that the residual pressure affects the detection of beam intensity fluctuations. Figure 15 shows the smallest detectable change in the number of particles entering the detector,¹⁸ ΔI , as a function of total beam intensity, I_b , for various residual chamber pressures, P_r . It can be seen that for a given beam intensity I_b , a change in P_r is directly proportional to a change in ΔI . Figure 16 shows the calculated beam intensity, I_b , as a function of beam length, L_D , for

Figure 15. ΔI as a Function of I_b for Different Residual Pressures.

¹⁸See March report (MLM-1250) for complete nomenclature used.

three source pressures. Extrapolated data from Figure 15 were used to obtain Figure 17, which gives the smallest detectable fractional change in beam intensity, Δf_b , as a function of total beam intensity for different residual pressures.

The foregoing information was used to obtain the set of practical working curves shown in Figure 18, which gives Δf_b as a function of beam length for different residual and source pressures. This plot allows a fairly accurate prediction as to the detection capabilities of this detector for a given beam length, residual pressure and source pressure. For example:

For a beam length between source and detector of 60 cm, a source pressure of 10^{-1} torr and a residual chamber pressure of 10^{-8} torr, a 6×10^{-5} (or 0.006%) change in the number of beam particles entering the detector can be seen.

A full scale crossed beam apparatus is being designed based on a conservative interpretation of these results. Theoretical calculations are being made for the determination of the expected intensity fluctuations, both classical and quantum mechanical, in an actual crossed beam experiment.

Collision Integrals The kinetic theory of Chapman and Enskog predicts the transport properties of a gas as functions of the collision integrals. The collision integrals, which are functions of the intermolecular potential between the molecules of the gas, must be calculated numerically. They have been calculated for a number of special potentials and these calculations have been used extensively in evaluating transport properties of gases. Evidence has been accumulating that indicates that these potentials are inadequate for describing the transport properties over a wide range of physical conditions. Thus, in recent years there has been a renewed interest in calculating these integrals for more flexible potentials.

Figure 16. Beam Intensity as a Function of Length for Different Source Pressures (calculated, assuming no residual scattering).

Figure 17. Δf_b as a Function of I_b for Different Residual Pressures.

Figure 18. Minimum Detectable Intensity Fraction (Δf_b) as a Function of Beam Length (l_D) for Different Source and Residual Pressures (P_s and P_r), (from extrapolated experimental data - run 23).

A computer program was written at Mound to calculate these integrals for a potential containing seven adjustable parameters. However, collision integrals calculated with this program differed significantly from published values (MLM-1227). A new program is being written which contains several features not present in the previous program. Instead of writing the program to use one potential with a large number of adjustable parameters, it is being written so that any potential function can be used (i.e. the potential function itself will be input data for the new program. Also, there are several similarities between the calculation of the collision integrals and the calculation of scattering cross sections for molecular beam experiments and the calculation of quantum mechanical collision integrals. The new program is being written as a series of sub-programs so that, wherever appropriate, the same sub-program could be used for all three calculations.

Since no theoretical discrepancies have been found in Mound's previous computations, the numerical techniques have been changed to improve the integrations. Gaussian Quadrature with appropriate weight functions is being used to evaluate numerically the integrals. For example, the integrand of the integral for the angle of deflection, namely

$$\int_{r_m}^{\infty} r^2 \left[1 - \frac{\phi(r)}{E} - \frac{b^2}{r^2} \right]^{-1/2} dr$$

has a singularity at $r=r_m$. This singularity can be removed by using a Gaussian Quadrature with a weight function of

$$\left(1 - \frac{r_m^2}{r^2} \right)^{-1/2}$$

With this weight function the integrand is a smooth function of the variable r_m/r . The advantage of using Gaussian Quadrature in the calculation of the collision integrals has been discussed fully by Smith and Munn.¹⁹

HELIUM VAPOR PRESSURE THERMOMETRY

Thermomolecular pressure data were collected by the differential pressure, two-tube method for a mixture of air and helium-4 with a cold temperature of 77°K to verify that some previous anomalous helium-3 data were in error due to the presence of air as an impurity. The data for both impure helium-3 and helium-4 were compared with the Weber-Schmidt equation²⁰ and with previous data for the pure gases with a cold temperature of 77°K. The tube radii used were 0.29 cm and 0.14 cm.

These data indicate clearly the necessity of working only with pure gases in these experiments. The observation (see Figure 19) that the experimental curves for the impure gases cross above the curve for the pure gases at low pressure suggests that the maximum $\Delta\Delta P$ for air must occur at a lower value of P_w than is the case with pure helium-3 or helium-4.

¹⁹J. Smith and R. J. Munn, *J. Chem. Phys.*, **41**, 3560 (1964).

²⁰S. Weber and G. Schmidt, *Leiden Comm*, No. 246C (1936).

²¹G. Hettner, *Zs. f. Phys.* **27**, 12 (1924).

²²S. Weber, *Leiden Comm*, No. 71B, 11-33 (1932).

Figure 19

Abscissa, P_w (0.29 cm), are the pressures measured in torr at the warm end of the 0.29 cm radius pressure sensing tube.

Ordinate, $\Delta\Delta P$ (0.14 cm, 0.29 cm), are the measured pressure differences in torr between the warm ends of the 0.14 cm and the 0.29 cm radius tubes. That is

$$\Delta\Delta P (0.14 \text{ cm}, 0.29 \text{ cm}) = P_w (0.14 \text{ cm}) - P_w (0.29 \text{ cm})$$

where it is assumed that

$$P_w (R) = P_c + \Delta P (R)$$

with P_c being the cold end or bulb pressure, ΔP is the thermomolecular pressure difference, and R refers to the individual tube radius. Thus,

$$\Delta\Delta P (0.14 \text{ cm}, 0.29 \text{ cm}) = \Delta P (0.14 \text{ cm}) - \Delta P (0.29 \text{ cm}).$$

The solid curve represents the predictions of the Weber-Schmidt equation.

The dashed curves represent smooth curves drawn through the various data points shown.

The open squares, $\square$, represent recent Mound measurements for pure helium-3 gas with $T_w = 302.8 \pm 0.1^\circ\text{K}$ and $T_c = 77.1 \pm 0.1^\circ\text{K}$.

The open circles, $\circ$ represent recent Mound measurements for pure helium-4 gas with $T_w = 303.5 \pm 0.3^\circ\text{K}$ and $T_c = 77.1 \pm 0.1^\circ\text{K}$.

The solid squares, $\blacksquare$, represent recent Mound measurements for a mixture of helium-3 and approximately 3 1/2% air with $T_w = 303.3 \pm 0.5^\circ\text{K}$ and $T_c = 76.8 \pm 0.1^\circ\text{K}$.

The solid circles, $\bullet$ represent the present data for a mixture of helium-4 and 4.87% air by mass spectrographic analysis with $T_w = 303.6 \pm 0.5^\circ\text{K}$ and $T_c = 77.1 \pm 0.1^\circ\text{K}$.

The differential equation describing the thermomolecular pressure difference effect, based on the model of Hettner²¹ and Weber²² was derived in two previous reports²³. This equation is

$$\frac{dp}{dT} = \frac{6\eta^2}{\rho T} \left[\frac{l}{r_o^2 + 4\gamma r_o} \right]$$

where γ is the "slip coefficient" defined by

$$\gamma = \sqrt{\frac{\pi}{2}} \sqrt{\frac{M}{RT}} \frac{\eta}{\rho}$$

In references 22 and 23 the term containing γ was neglected to separate the variables and obtain an explicit solution to the differential equation.

The differential equation is homogeneous if a rigid sphere molecular model is employed for the viscosity, and may be solved by a simple transformation which allows the variables to be separated. The integral expressions may be evaluated analytically and lead to a logarithmic equation, similar to that of Weber-Schmidt, which must be solved by numerical methods.

Using the ideal gas relation

$$\rho = pM/RT$$

and the equation for the viscosity of a gas consisting of rigid spheres of diameter σ , yields the homogeneous differential equation

$$\frac{dP}{dT} = \frac{75}{16} \frac{R^2}{\pi \sigma^2 N} \left[\frac{T}{8r_o^2 \sigma^2 N p + 5\sqrt{2} R r_o T} \right]$$

This is of the form

$$\frac{dP}{dT} = \frac{CT}{Ap + BT}$$

By letting $p = \xi T$, from which $dp = \xi dT + T d\xi$, the differential equation transforms to

$$\int_{T_1}^{T_2} \frac{dT}{T} + \int_{\xi_1}^{\xi_2} \frac{A\xi + B}{A\xi^2 + B\xi - C} d\xi = 0$$

which may be integrated analytically. Since $\xi_1 = P_1/T_1$ and $\xi_2 = P_2/T_2$ the equation can be transformed back to the original variables of pressure and temperature. The final expression for the thermomolecular pressure effect, in terms of the pressures and temperatures at the ends of the tube, is

²³MLM-1231 and MLM-1254.

$$\ln \frac{T_2}{T_1} = \frac{1}{2} \ln \left(\frac{8r_o^2 \sigma^2 N p_1^2 / T_1^2 + 5\sqrt{2} R r_o P_1 / T_1 - 75 R^2 / 16 \pi \sigma^2 N}{8r_o^2 \sigma^2 N p_2^2 / T_2^2 + 5\sqrt{2} R r_o P_2 / T_2 - 75 R^2 / 16 \pi \sigma^2 N} \right) +$$

$$\frac{\sqrt{\pi}}{\sqrt{4\pi + 12}} \left\{ \ln \left(\frac{16r_o^2 \sigma^2 N p_1 / T_1 + 5(\sqrt{2} - \sqrt{2 + 6/\pi}) R r_o}{16r_o^2 \sigma^2 N p_2 / T_2 + 5(\sqrt{2} - \sqrt{2 + 6/\pi}) R r_o} \right) - \right.$$

$$\left. \ln \left(\frac{16r_o^2 \sigma^2 N p_1 / T_1 + 5(\sqrt{2} + \sqrt{2 + 6/\pi}) R r_o}{16r_o^2 \sigma^2 N p_2 / T_2 + 5(\sqrt{2} + \sqrt{2 + 6/\pi}) R r_o} \right) \right\}$$

where T_1, P_1 = cold temperature and pressure

T_2, P_2 = hot temperature and pressure

r_o = radius of capillary

σ = rigid sphere collision diameter

N = Avagadro's number

R = universal gas constant

ANALYTICAL AND INSTRUMENTATION

Methods of analyzing elements and compounds are being developed to support the programs at Mound Laboratory. These methods include instrumental techniques and standard wet methods.

NEUTRON ACTIVATION ANALYSIS

Impurities in High Purity Boron A zone-refined bar of high purity elemental boron, received from the New Brunswick Laboratory (NBL), was examined by neutron activation analysis in order to determine the homogeneity. The boron, to be used for rod samples to be distributed between interested AEC contractors, was examined for impurities by neutron activation analysis.

Contamination of the sample while grinding was also investigated by comparing a sample of original zone refined elemental boron with the same material powdered in a steel mortar and pestle. The samples were irradiated in front of the target for five minutes at a flux of 2×10^{10} n/cm²/sec. Immediately, the samples were counted for five minutes, decayed for 15 minutes and recounted for five minutes.

Impurities (semi-quantitative) found in both samples were as follows: 100 - 200 ppm silicon and 0.3 - 0.7 percent nitrogen. The sample powdered in the mortar was contaminated with about 500 ppm iron.

For an impurity variation in a rod of elemental boron, silicon would be the most selective element with a detectable limit of about 20 ppm on a five gram sample, while nitrogen would be the most accurate due to its high count rate. A different procedure is required for powdering the boron since steel introduces many impurities.

From the above information, it is possible to nondestructively determine the homogeneity of pieces cut from a high purity zone refined elemental boron rod by neutron activation analysis. This procedure could be used to determine the homogeneity of samples sent to interested AEC contractors for interlaboratory comparisons.

CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM-IRON-NICKEL SOLUTIONS

A procedure has been developed for the determination of uranium and iron in solutions containing nickel. The following is a brief outline of the suggested procedure:

1. Place a 5-g sample (accurately weighed) in a one-liter volumetric flask containing 30 ml conc HNO₃. After sample dissolution, dilute the mixture to the mark with 1 N H₂SO₄.
2. Transfer a 1-ml aliquot to a mercury-cathode cell, and add 2-3 ml 1 N H₂SO₄.
3. Add 5-8 drops of saturated sulfamic acid, and carefully purge the sample, without mechanical stirring, for ten minutes.
4. Partially reduce the total uranium-iron content at -0.005 volt vs. standard calomel electrode (SCE), and then finish the reduction at -0.350 volt. (After the reduction has started, turn on the mechanical stirrer.
5. Transfer a 2-ml aliquot of the sample to a Pt-gauze cathode cell.
6. Add 5-8 drops of saturated sulfamic acid, 20-30 ml 1 N HCl, and purge the solution for 5 minutes.

7. Reduce the iron to +0.270 volt vs. SCE.

The first readout voltage (obtained with the mercury-cathode cell) represents the total uranium-iron content, whereas the second readout represents only the total iron. The difference between the readouts represents the uranium content.

On a standard uranium-iron-nickel sample, a series of determinations were made; 10 for iron and 12 for uranium-iron. The results may be summarized as follows:

<i>Constituent</i>	<i>Theory (g/Sample Wt.)</i>	<i>Calc.</i>	<i>Relative Error (%)</i>	<i>Relative Deviation (%)</i>
Fe	0.9400	0.9411	+0.11	±0.30
U	0.5794	0.5768	-0.14	±0.20

A single determination of the iron and uranium content of the sample may be made in 30 minutes.