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I. INTRODUCTION

Personnel who are working with radioactive materials are constantly monitored in order to determine the amount of their exposure to these materials. One type of monitoring is the assay of urine to determine the amount of radioactive material being excreted by this means. The procedure employed for this assay is described in this report, and data to show its performance and reasons for its present course are presented. The method is used in monitoring a permissible polonium excretion of 500 disintegrations per minute per 24-hour urine sample. This permissible level corresponds to 8 counts per minute per 50 milliliters of urine.

II. STANDARD PROCEDURE

When acid solutions of polonium are allowed to come in contact with certain metals, the polonium is attached in large portion to the metal. This plating process and the determination of the amount of polonium present on the metal by counting the alpha particles emitted is the basis of the method for assay of urine for polonium.

Urine samples are collected in half-pint Sealright paper cartons containing a small amount of sulfamic acid. At the time of assay (within a few hours of collection) 50-milliliter urine samples are poured after thorough shaking into waxed paper cups and brought to an acid normality of one by the addition of 10 milliliters of six normal hydrochloric acid. One-inch diameter

copper discs (16 gauge) on glass hooks are suspended in the solutions which are then stirred for a two-hour period with glass stirrers. The copper discs are removed, dried, and the alpha particles emitted by attached polonium are counted in parallel plate alpha counters. Each side of the disc is counted for 20 minutes; the sum of the counts on the two sides measures the amount of polonium extracted. Figure 1 is a diagram of the plating setup.

III. EFFICIENCY AND CHARACTERISTICS OF THE METHOD

The procedure described above is used because it is most suitable for the routine assay used at Mound Laboratory. It recovers or measures 86.1 per cent $\pm$ 11.9 per cent of the polonium which may be present in urine solutions. This recovery depends upon the polonium concentration, the time of extraction and the surface area of the extracting disc. Polonium concentrations above 200 counts per minute per 50 milliliters of solution are not recovered as efficiently. Below 200 counts per minute per 50 milliliters the concentration has no detectable effect on recovery. A three-hour plating period extracts maximum amounts of activity. No increased recovery occurs from longer extraction times, but a significantly smaller per cent is recovered in less time. Two-hour extractions are used routinely, however, because the difference in per cent recovery is not great enough to justify the greater amount of time required for the increased recovery at three hours. One-inch discs are used in preference to three-quarter inch discs because the greater surface area removes a greater percentage of polonium. Under our conditions copper discs recover more polonium than do silver discs.

FIGURE 1

Recovery is affected also by the amount and type of agent used to acidify the urine. Hydrochloric and nitric acids allow better polonium recovery than do a variety of other acids tested. Solutions adjusted with hydrochloric acid to normalities varying between 0.5 and 1.5 give equally good recoveries. At high acidities and long plating times, apparently the release of copper ions into the urine solution decreases polonium recovery.

Discs used for polonium extraction must be clean and unscratched. In order to obtain a clean smooth surface, discs are dipped into hot concentrated nitric acid and then into water. This dipping is repeated using two water washes. The disc is next dipped into concentrated hydrochloric acid and washed in two water baths. It is then air dried after being dipped into two ethyl alcohol baths followed by two ether baths. This method is simpler and produces better results than several other methods which have been tried. After extracting polonium from urine, the discs must be dried for counting. This should be done without loss of activity and without contamination. The discs are first rinsed in tap water and then dried either under an infrared lamp, in air after dipping them into alcohol and then ether, or in air after blotting with Kleenex. The air-drying method after blotting with Kleenex is used routinely.

Urine, too, must be handled properly. If collected urine samples are allowed to stand for any appreciable time before assay, higher polonium recoveries could be made than by the present method if 200 milligrams of sulfamic acid rather than 50 milligrams was used in the container. This change may reduce loss caused by adherence to container walls or by precipitation. If urine is allowed to stand so that a precipitate occurs a good proportion of the polonium present is combined with the precipitate and is not recovered by the routine technique.

IV. DETAILED RESEARCH ON THE METHOD

The data on these urine assays have been collected by various laboratory workers over a considerable period of time and have been selected from a large accumulation of figures. A great deal of the work was done at an early period in the history of the laboratory. Consequently, some of the data were secured with aims in mind which are not necessarily being emphasized at the present time. Moreover, a great deal of experimental work, not included in this report, was done with aqueous polonium-hydrochloric acid solutions. As a consequence of these factors, there is not always as much usable data concerning any particular question as is desirable. Those data, however, which are applicable to our present procedure, are recorded in this report and have been collected here primarily to clarify procedural questions. A number of possible theoretical implications have been put aside for other investigations. Work dealing with related problems has been presented in Rochester Report MDDC-7188.

Some of the possibilities for error in these experiments might be mentioned at this point. Machine background counts are determined as the average of the count during the previous night. It is conceivable that daytime fluctuations are not measured as closely as possible in this manner and that discs counted on different days, which occurred in most experiments, or at different times may be in error due to improper background correction. No direct data are available to correct for or to estimate such error. In general the machine backgrounds run quite consistently for periods of days. It is unlikely, therefore, that unmeasured changes can cause any large error. At present, in new quarters, machine operation is very consistent; better than it was while these experiments were run. Since consistency has been improved, it is prudent in this work that counts close to zero or comparative counts

showing very small differences be carefully evaluated in determining significance. Along with this possible counting error is the practice in these experiments of recording minus counts, possible because of background, as zero counts. In precounting assay discs or in making counts close to zero this technique may introduce serious error into the data.

The task of making up urine solutions containing known amounts of polonium introduces another source of error if comparative assays are not run on the same solution. Accurate preparation of solutions containing small amounts of polonium is difficult. Large dilutions may introduce considerable error; direct determinations on low count solutions are probably best. Some discussion of this matter is given below in the section on standardizing stock solutions. The use of urine artificially activated rather than urine obtained from individuals who have ingested polonium also may bias to some extent the recoveries obtained.

Alternative methods of assay which have been attempted have proved inefficient or impractical. Such methods which have been studied briefly include coprecipitation and electrolysis of the polonium from water polonium-hydrochloric acid solutions.

A. General Techniques

1. Standardization of Stock Solutions

Two matters of importance in the study of assay methods for polonium in urine are radioactive contamination and radioactivity measurements. The problems of avoiding contamination, though continuous and many, will not be discussed in this report. A short discussion only concerning measurement, not from a counting instrument standpoint, but from a solution handling standpoint, will be given.

Measurement is involved in this research in the need to know the amount of activity that is being worked with. In general, known amounts of polonium are added to pooled urine collections, and on aliquots from such preparations the various experimental determinations are made. In the early assay research, the amount of activity added to the urine was determined by plating the polonium from the urine onto copper discs in the manner described above. By this method, two 3-hour platings with different one-inch discs, or three 2-hour platings with different one-inch discs from 0.5 normal hydrochloric acid solutions give determinations which compare well with the alternative glass slide method.

The glass slide method has also been used to determine the amount of activity in a solution. Portions of water-acid solution containing polonium are spread on square glass microscope slides, dried under a heat lamp, coated with collodion, and the emitted alpha-rays counted. The portions of solution are measured by means of lambda pipettes. The very small amounts of activity worked with in this research argued first against the use of the glass slide assay of stock solutions but, with proper precautions, it works extremely well. Dilution of usual stock solutions used in other research, with a consequent calculation of the amount of polonium present is not a satisfactory technique because of the great dilution factor necessary. However, dilution of much less concentrated stock solutions with urine provides a dependable technique for calculating the polonium content of the urine-polonium solution.

The following figures are a comparison of the two methods described above. Aliquots of a hydrochloric acid stock solution of polonium were dried on glass slides and counted. A portion of this stock solution was also diluted 1:50 with a urine sample, made 0.5 normal with hydrochloric acid, and assayed

with copper discs. Three different one-inch copper discs were each used for a two-hour period in the extraction. Table I shows that the amounts of polonium determined by the two methods give equally usable results.

Table I

POLONIUM MEASUREMENTS BY GLASS SLIDE AND COPPER DISC TECHNIQUES

<u>Glass Slides</u>		<u>Copper Discs</u>	
<u>No. of Samples</u>	<u>Recovery</u>	<u>No. of Samples</u>	<u>Recovery</u>
8	17.17 ± 0.495 c./min./0.5 ml. or 34.34 c./min./ml.	20	34.01 ± 2.11 c./min./50 ml.

2. Cleaning Copper Discs

The copper discs used in plating are stamped out by the laboratory machine shop. Consequently, they are obtained dirty (oil, grease, etc.) and frequently scratched. Discs with large scratches must be discarded since the scratch may affect the alpha particle count. Other discs must be cleaned to remove dirt and to leave a surface as smooth as possible, as well as to produce a disc with the lowest possible activity count. By the cleaning methods used in these experiments all but approximately 0.5 counts per minute per disc is removed. This count is primarily the natural activity of the metal.

Various disc cleaning methods have been used. These methods are as follows:

a. Flame disc to red heat, quench in ethyl alcohol. Dip into hot concentrated nitric acid, then into water; again into hot concentrated nitric acid, and then into two water baths. Next, dip into concentrated hydrochloric

acid and then into five different water baths. Air dry the disc after dipping into two ethyl alcohol baths and then two ether baths.

b. Same as Method a. except that the disc is quenched in methyl alcohol.

c. Same as Method a. except that the flaming and quenching is not performed.

d. Method a. is varied by quenching in dilute hydrochloric acid, and, after the concentrated hydrochloric acid bath, the disc is rinsed in running tap water and then dried with three baths each of ethyl alcohol and ether.

e. Same as Method c. except that running tap water is used after the concentrated hydrochloric acid bath and three baths each of ethyl alcohol and ether are used.

In an experiment, in which each of these methods of cleaning was used, the counts remaining on the discs are shown in Table II.

Table II

NUMBER OF COPPER DISCS CARRYING VARIOUS ALPHA COUNTS
AFTER DIFFERENT METHODS OF CLEANING

<u>Count</u>	<u>Cleaning Method</u>				
	<u>a.</u>	<u>b.</u>	<u>c.</u>	<u>d.</u>	<u>e.</u>
0	12	7	11	13	12
0 to 1/2	8	13	6	2	1
1/2 to 1	6	2	1	3	0
1 or greater	<u>11</u>	<u>1</u>	<u>6</u>	<u>19</u>	<u>4</u>
Total discs	37	23	24	37	17

Because zero counts in the above table include minus counts (possible, because of background), the actual minus counts not being recorded, it is not possible to calculate a mean count for the various methods. If it is assumed, however, that at zero count an equal number of minus and plus counts would be obtained, then a test of departure from this distribution toward plus counts would show that an actual count was being obtained. (Including minus and zero counts together would slightly bias the test toward minus counts, a fact which would only make more definite a significant trend to positive counts.) A chi square test comparing plus and zero counts for each of the methods shows a significant number of plus counts in some cases. Methods c. and e. show the lowest chi square values. This result suggests that these methods produce discs with fewest positive counts. It should be pointed out, however, that the low counts in this work are especially subject to the counting error (background change) mentioned previously and also that recording minus counts as zero counts could in this case introduce a very serious error.

These particular comparisons do not offer a conclusive answer to the question of the best cleaning method but they do allow a selection of method not entirely arbitrary. Method c. has been simplified by using only two water baths after the hydrochloric acid bath and is the method now used routinely.

3. Drying Copper Discs

After the plating process, the copper discs must be dried before counting. Three methods of doing this have been used. The discs are first rinsed in water. They are then dried either under an infrared lamp, in air after dipping them in anhydrous alcohol and then anhydrous ether or in air after blotting with Kleenex. The solvent method has several advantages.

In an experiment to compare the infrared and the solvent method, six liters of urine were pooled in a large glass container, and sufficient polonium was added to give approximately 30 counts per minute per 50 milliliters. Hydrochloric acid was added to make the solution one normal and the mixture was agitated for an hour. One hundred and ten 50-milliliter aliquots were then extracted for two hours with one-inch copper discs. After plating, half of the discs were dried for 30 minutes with a heat lamp, and half were dried by dipping into two alcohol baths and then into two ether baths. The discs were counted 20 minutes per side in the parallel plate counters. The counts obtained are given in Table III and show that these drying methods obviously do not result in different final counts.

Table III

POLONIUM RECOVERY (c./min./50 ml.) BY DIFFERENT DRYING METHODS

<u>Heat Drying</u>	<u>Solvent Drying</u>
25.5 $\pm$ 2.93	26.0 $\pm$ 2.71

As a check for polonium loss, the wash water from the infrared dried discs as well as the water, alcohol, and ether from the solvent dried discs were assayed. No significant counts were obtained from any of these solutions thus showing no loss by either method and confirming the similar recoveries of polonium shown in Table III.

In another experiment to check polonium loss in drying solvents, a liter of alcohol and a liter of ether which had been used for drying many discs was acidified and assayed. Table IV shows the results. Because of the very low count it would be difficult to attach significance to either of these recoveries and it can be concluded that an insignificant amount of polonium is lost in drying solvents.

Table IV

POLONIUM RECOVERY FROM USED DRYING SOLVENTS

<u>Solution</u>	<u>No. of Samples</u>	<u>c./min./100 ml. Recovered</u>
Alcohol	20	0.23
Ether	20	1.45

Recently, in new air conditioned laboratories, it has been found that discs dry quickly and cleanly in the air after blotting with Kleenex. Though no recovery comparisons have been made including this method, it is the one used routinely at present.

4. Other Factors

In all assays the polonium extractions were made at room temperature. The stirrers used in agitating the solutions rotated at speeds varying between 150 to 700 revolutions per minute with no apparent effect upon the efficiency of extraction.

B. Handling Procedures for Urine

Individual urine samples are collected in cylindrical half-pint Seal-right paper containers (Serial No. A-9) and transferred in these containers to the Routine Urine Analysis Laboratory. Fifty milliliters of sample is then transferred to a waxed paper cup from which the polonium is extracted onto a copper disc as described previously. Different amounts of time may elapse between collection and assay. During this time polonium might be lost from the sample onto the container; also, changes in the urine itself may occur, resulting in a precipitate, which could be responsible for a redistribution of the activity in the sample and so a different

assay result. A series of experiments was run to evaluate some of the factors involved in these possible losses.

1. Polonium Loss after Urine Collection

In an experiment to measure possible loss, different amounts of polonium were added to two batches of pooled urine after which the solutions were stirred for one hour. Some aliquots from this stock solution were then assayed immediately while other aliquots were allowed to stand in Sealright paper containers to which approximately 65 milligrams of sulfamic acid had been added (see below). After standing for varying amounts of time with occasional shaking, 50-milliliter samples from these containers were also assayed. The 50-milliliter sample in each case was placed in a paper cup, five milliliters of six normal hydrochloric acid was added and the sample was then extracted for two hours with one-inch diameter copper discs. Table V summarizes the data obtained in this way.

Table V

POLONIUM RECOVERY FROM URINE AFTER STANDING FOR VARIOUS PERIODS OF TIME

<u>Po Added</u> <u>c./min./50 ml.)</u>	<u>No. of Samples</u>	<u>Time Allowed to</u> <u>Stand (Hours)</u>	<u>Recovery</u> <u>(c./min./50 ml.)</u>
36.35	20	0	24.52
36.35	20	4	22.88
36.35	20	24	21.90
36.35	20	48	18.16
36.35	20	72	16.59
251.75	30	0	158.84
251.75	30	4	153.83
251.75	30	24	125.63
251.75	30	48	102.84
251.75	30	72	96.57

Assuming the zero hour extraction to be the total amount recoverable, the other figures show the reduced recovery due to standing. Loss in four hours does not appear to be serious. In 24 hours, however, the loss has become greater, especially at the higher polonium level. Still lower recoveries are obtained following longer standing periods. Considerable leakage from the cartons also occurs after long periods of standing.

A check on the possibility of polonium adherence to the carton was run by cutting discs, 7/8 inches in diameter, from the bottom and top of cartons which had contained a polonium-urine solution for various amounts of time and counting these discs for radioactivity. The counts were very low; consequently, their significance was not evident. The work has not been repeated. Some of the polonium loss shown in Table V probably is onto the container walls; though precipitates, as shown below, may account for it. The work with precipitates, however, has involved longer periods of time so that there is no clear cut answer as to which of these factors account for the loss.

2. Sulfamic Acid Effect

It is conceivable that by acidifying the urine sample, loss due to adherence to the container or to precipitation would be reduced. If the acid concentration, however, is too high the paper container will be affected and leaks will result. Sulfamic acid has been used in the past as an acidifying agent. Approximately 50 milligrams is routinely placed in collection cartons. An evaluation of this practice using various amounts of sulfamic acid per 100 milliliters of activated urine was made. The samples were allowed to stand for 20 hours and then extracted with one-inch copper discs for two hours. Fifty

samples assayed at the time polonium was added to the urine averaged 15.9 counts per minute per 50 milliliters. Recoveries after 20 hours from samples containing sulfamic acid are shown in Table VI.

Table VI

EFFECT OF SULFAMIC ACID ON POLONIUM RECOVERY

<u>Sulfamic Acid per 100 ml. urine (grams)</u>	<u>Approximate pH of Samples in Cartons</u>	<u>No. of Samples</u>	<u>Activity Extracted (c./min./50 ml.)</u>
0.05	6	50	11.2
0.20	5	50	15.4
1.00	1.7	50	8.6*
1.50	1.5	50	8.2*
2.00	1.3	50	6.8*

* Some sample loss by leakage.

The high pH of the samples at the low levels of sulfamic acid precludes a preservative effect from a bacterial standpoint, and at higher acid levels it is seen that polonium recovery is decreased. The lower recovery could be due to a sulfamic acid effect or possible to sample leakage.

This experiment was repeated using amounts of sulfamic acid from 0 to 500 milligrams per 100 milliliters of urine solution. (Solutions containing more than 200 milligrams were lost because of leakage.) Table VII shows the results.

Table VII

SULFAMIC ACID EFFECTS ON POLONIUM RECOVERY

<u>Sulfamic Acid</u> <u>(mg.)</u>	<u>Counts per minute per 50 ml.*</u>				<u>Standing</u> <u>Time</u> <u>(Hours)</u>
	<u>Run</u> <u>No. 1</u>	<u>Run</u> <u>No. 2</u>	<u>Run</u> <u>No. 3</u>	<u>Run</u> <u>No. 4</u>	
0	18.3	18.1	18.3	16.9	0
0	13.1	11.7	3.2	14.3	20
100	18.5	15.3	12.4	14.7	20
200	17.0	22.0	20.2	20.4	20

* Values are means of five samples, except those assayed immediately which are means of nine samples.

Statistical analysis of these data shows that a difference between the recoveries obtained in different runs exists. Analysis also shows that the presence of sulfamic acid has an effect on recovery and that this acid at a concentration of 200 milligrams per 100 milliliters increases significantly the recovery of polonium from urine which has been standing for a period of 20 hours.

3. Distribution of Polonium Between Precipitate and Liquid Phase in Urine after Prolonged Standing

Polonium recovery from urine solutions allowed to stand frequently decreases at a greater rate than can be accounted for by radioactive decay. This holds true between pH's one to seven and is not appreciably affected by stirring. The following work was done in an attempt to account for this loss.

Polonium in 0.5 normal hydrochloric acid was added to pooled urine (4,500 milliliters) to bring the count to 32.78 counts per minute per 50 milliliters. The solution was adjusted to pH 2.0 with concentrated hydrochloric acid

by use of a Beckman meter. After stirring for one-half hour, twenty-five 50-milliliter aliquots were taken, acidified to one normal, and extracted for three hours with one-inch diameter copper discs. The remainder of the urine was allowed to stand undisturbed for 48 days during which time a precipitate formed. At the end of this period 3,000 milliliters of solution was made up to 3,600 milliliters and one normal by the addition of hydrochloric acid and water. After stirring for 24 hours the solution was divided into 1,800-milliliter portions. Twenty-five 60-milliliter (50 milliliters of urine) aliquots from one of these portions were extracted as above. The other portion was run through a Gooch filter. Sixty-milliliter aliquots of the filtrate were extracted as well as similar aliquots from a solution obtained by dissolving the precipitate in 12 normal hydrochloric acid and diluting to 1,800 milliliters with water. Results were as shown in Table VIII.

Table VIII

POLONIUM RECOVERY FROM URINE PRECIPITATE

Extracted Immediately After Preparation c./min./50 ml.	From Whole Solution c./min./50 ml.	48 Days after Preparation			Filtrate Recovery + Precipitate Recovery c./min./50 ml.
		From Filtrate c./min./50 ml.	From Dissolved ppt. c./min./50 ml.		
25.8*	16.9*	10.4	17.4		27.8

* Value from secondary report.

These data show that the precipitate which forms in a urine solution combines polonium with it which is not recovered by the standard plating procedure. Decreased recovery with increased standing time obviously can be due to such combination.

C. Disc Material

Little information is available on the use of different metals for the purpose of extracting polonium from urine solutions. Copper discs have been used at the Mound Laboratory. In the following experiment, a comparison of the extracting efficiency of copper and silver discs is made.

Solutions of polonium in pooled urine were made up to contain 23.3 counts and 910 counts per minute per 50 milliliters respectively. Forty one-inch copper discs and forth one-inch silver discs were cleaned and precounted, and the solutions at each level were extracted with these discs for two hours using 20 samples in each case. The recoveries, corrected for decay, are given in Table IX.

Table IX

POLONIUM RECOVERY BY COPPER VS. SILVER DISCS

<u>Polonium Concentration</u> <u>(c./min./50 ml.)</u>	<u>Disc</u> <u>Material</u>	<u>No. of</u> <u>Discs</u>	<u>Recovery</u> <u>(c./min./50 ml.)</u>	<u>Recovery:Per Cent</u> <u>of Polonium Added</u>
23.3	Copper	20	19.8	85.0
23.3	Silver	20	17.3	74.1
910.0	Copper	20	586.0	64.4
910.0	Silver	20	452.0	49.6

An analysis of variance of the per cent recoveries of the individual discs shows that very significant differences exist between the recoveries for the metals and between recoveries for the two polonium concentrations. Interpreting this in terms of the means of Table IX it is seen that copper discs extract a significantly greater amount of activity than do silver discs and, also, that a significantly greater per cent of the activity present is removed at the lower

polonium concentration. The latter result might well be expected on the basis of replacement or attachment rates. The greater efficiency of the copper compared to the silver discs substantiates their use for urine assay.

D. Acidification of Urine for Plating

In order to maintain the polonium in a urine sample in a condition which will allow it to become attached to a copper disc, it is necessary that the solution be acid. It is possible to make urine acid with a variety of agents and it is also possible to secure various degrees of acidity. The type of acid and the degree of acidity are factors which affect the efficiency of extraction. Various experiments to determine the most favorable conditions of acidity have been run.

1. Types of Acid

In earlier work on aqueous polonium-hydrochloric acid solutions it was found that hydrochloric, hydrobromic, and nitric acids were most efficient for extraction as compared with sulfuric, acetic, iodic, and phosphoric acids. In the following experiment hydrochloric, hydrobromic, and nitric acids are compared when used with urine.

Equal portions of pooled urine, made to contain approximately 30 counts per minute of polonium per 50 milliliters, were acidified to one normal with hydrochloric acid, hydrobromic acid, and nitric acid respectively. Sixty 50-milliliter aliquots of each of these solutions were then extracted for two hours with one-inch diameter copper discs. The results shown in Table X were obtained.

Table X

POLONIUM RECOVERIES IN THE PRESENCE OF DIFFERENT ACIDS

<u>Acid</u>	<u>(c./min./50 ml.)</u>
Hydrochloric	24.6
Nitric	25.4
Hydrobromic	16.8

Recovery with hydrobromic acid is obviously lowest. A t test comparison of the recoveries with hydrochloric and nitric acids indicated the difference between the two to be not significant. (Counts were made on different days.) Neither acid, therefore, can be said to give better recoveries than the other. Hydrochloric acid is used routinely in urine assays.

2. Degree of Acidity

In preliminary work on this matter with aqueous polonium-hydrochloric acid solutions and hydrochloric acid as the acidifier, it was found that normalities from 0.1 normal to one normal gave best extraction in three hours. Recoveries decreased above one normal. A pilot experiment using urine (normalities from 10^{-7} to 1.5 adjusted with hydrochloric acid and both two and three hour extractions) showed greatest recoveries from 0.1, 0.4, and 0.8 normal solutions.

In a larger experiment, polonium was added to pooled urine so that it contained approximately 11 counts per minute per 50 milliliters. Various amounts of acid were added to secure different normalities and three different acids were used. Two and three-hour platings with one-inch diameter copper discs were made. The recoveries are shown in Table XI. Twenty samples were averaged for each recovery shown.

Table XI

POLONIUM RECOVERIES FROM DIFFERENT ACIDS AND DIFFERENT DEGREES OF ACIDITY

<u>Normality</u>	<u>pH</u>	<u>HCl</u> Recovery (c./min./50 ml.)		<u>pH</u>	<u>HNO₃</u> Recovery (c./min./50 ml.)		<u>pH</u>	<u>HBr</u> Recovery (c./min./50 ml.)	
		<u>2 Hours</u>	<u>3 Hours</u>		<u>2 Hours</u>	<u>3 Hours</u>		<u>2 Hours</u>	<u>3 Hours</u>
0.01	4.2	2.13	2.80	4.4	1.53	1.13	4.4	1.67	2.47
0.02	3.6	2.66	3.57	2.9	0.91	1.46	3.9	1.68	1.62
0.05	2.3	5.48	5.47	2.2	2.50	3.24	2.8	2.53	3.04
0.1	1.5	8.71	9.52	1.6	4.94	5.93	2.1	6.35	8.24
0.3	0.7	10.54	6.66	1.1	6.98	7.83	1.8	8.58	8.88
0.5	0.4	10.06	7.64	0.8	8.23	9.66	1.5	8.06	6.18
0.75	0.3	8.24	7.17	0.6	7.87	9.14	1.4	7.41	3.34
1.0	0.1	9.39	6.43	0.5	8.42	9.26	1.2	6.72	3.77
2.0	-	5.82	3.54	0.2	8.92	9.26	1.0	4.73	3.05
2.7	-	4.30	2.22	-	7.03	5.74			
2.6							0.4	5.45	3.70

These data show that recoveries with hydrochloric acid and hydrobromic acid are highest in solutions between 0.1 and one normal. Nitric acid recoveries are high even at a normality of 2.0. With hydrochloric acid and hydrobromic acid, high recoveries in three-hour platings are obtained at lower normalities than in two-hour platings, while with nitric acid highest recoveries occur in three hours at the same normalities as at two hours. The decreased recovery at longer plating times and higher normalities is discussed further on succeeding pages. The higher recoveries shown with hydrochloric acid and nitric acid as compared with hydrobromic acid bear out the data presented above.

1.17 7 2

In another experiment, normalities as well as more plating times were compared. The different normalities were established with different polonium stock solutions, in this case by somewhat greater dilution than usual (1:2,000). A comparison of recoveries for different normalities, therefore, includes the possible dilution error involved. The solutions contained 25.8, 27.8 and 24.2 counts per minute per 50 milliliters at 0.5, 1.0, and 1.5 normalities, respectively. The mean percentage recoveries for ten 50-milliliter aliquots at the different normalities and for different plating times are given in Table XII. One-inch copper discs were used.

Table XII

PERCENTAGE POLONIUM RECOVERIES AT DIFFERENT NORMALITIES AND PLATING TIMES

<u>Plating Time (Hours)</u>	<u>Normality (HCl)</u>		
	<u>0.5</u>	<u>1.0</u>	<u>1.5</u>
1/2	34.9	47.1	50.8
1	67.7	63.3	71.5
2	83.8	76.6	81.0
3	86.6	88.8	81.8

These data in Table XII show several interesting relationships regarding the normality range used. These are: 1.) In one-half hour, significantly better recoveries are obtained at normalities of 1.0 and 1.5 than at 0.5. 2.) In one hour, a better recovery is obtained at a normality of 1.5 than at 1.0. 3.) No significant effect due to normality occurs in two-hour extractions. 4.) In three hours a lower recovery is obtained at a normality of 1.5 than at 1.0.

Because of possible dilution errors mentioned previously, differences which approach significant levels closely may not be properly evaluated. However, no differences in recovery at normalities from 0.5 to 1.5 are demonstrated to occur in the standard plating time of two hours.

E. Plating Time

The time during which the disc is maintained in the urine solution is a factor which influences greatly the amount of polonium recovered. It is desirable that the greatest percentage of polonium present be recovered in the shortest time possible. Various experiments have been run in order to determine the optimum time for plating.

The results presented in the section directly above provide data on the question of optimum plating time. It is seen that recovery at three hours is greater than at two hours at each normality and that recovery at two hours is greater than at one hour. These differences are significant except those between two and three hours at 0.5 normal and at 1.5 normal. The reason for the lack of significance at 0.5 normal is not evident; at 1.5 normal it may well be caused by the removal of copper from the disc into the solution. This copper effect has been noted in other work and some data on it will be presented below. In this experiment then, at 1.0 normal, three hours gave the greatest recovery. At other normalities two or three hours gave good recovery. In all cases the longer plating times gave the best recovery or recovery equal to any shorter time period.

In another experiment, hydrochloric, hydrobromic, and nitric acids were used to bring the polonium-urine (approximately 32 counts per minute per 50 milliliters) solutions to 0.5 or 1.0 normality. The solutions were then extracted for various periods of time with one-inch diameter copper discs. For each

combination of variables (i.e. acid, time, normality) urine solutions were made up separately in one liter flasks and then divided into 20 aliquots. The per cent recoveries obtained are presented in Table XIII.

Table XIII

PERCENTAGE POLONIUM RECOVERY FOR DIFFERENT EXTRACTION TIMES

Extraction Time (Hours)	Per Cent Recovery					
	<u>HCl</u>		<u>HNO₃</u>		<u>HBr</u>	
	<u>0.5 N</u>	<u>1.0 N</u>	<u>0.5 N</u>	<u>1.0 N</u>	<u>0.5 N</u>	<u>1.0 N</u>
1	58.2	51.2	42.4	45.9	44.8	44.8
2	82.1	79.1	64.7	74.4	71.4	65.5
3	86.5	86.5	71.1	82.5	74.8	66.4
4	84.0	81.3	73.2	87.4	77.8	73.0
5	85.6	83.2	75.9	83.1	68.6	64.7
6	84.3	84.1	78.2	85.1	63.4	57.3

These results bear out the data presented above in a comparison of the three acids. Hydrochloric and nitric acids give higher recoveries than does hydrobromic acid. They also confirm the statement that hydrochloric acid normalities in the range of 0.5 to one normal make little difference in recovery. And they bear out the data given directly above by showing in the case of hydrochloric acid (also nitric acid) an increase in recovery between two and three-hour platings. Still longer plating times in no case give consistently greater recoveries. At a normality of 1.0, then, using hydrochloric acid, a higher per cent recovery is made in a three-hour extraction period than in a two-hour period. Longer extraction periods, however, do not further increase recovery.

It has been noted that the amount of copper ion (Cu^{++}) increases with time in plating solutions. To determine whether this ion has an effect on polonium recovery, a series of recovery runs was made for various time intervals, with one-inch diameter copper discs, with and without the addition of cupric chloride to dilute hydrochloric acid-polonium solutions. One milliliter of a solution containing 0.0258 grams of copper chloride per milliliter was used for copper additions. This amount was intended to give a 10 to 1 excess of cupric chloride over that normally formed in a three-hour run.

Of the eleven platings without addition of copper, the average count per minute recovered was in 10 cases higher than the average recovery at similar plating times with copper added. A chi square test shows this to be a significant departure from the expected half higher and half lower averages if no effect due to copper existed. It can be concluded, therefore, that excess copper ions in a plating solution will tend to reduce polonium recovery. Higher than usual copper ion concentrations can occur with high acid normalities and long extracting times.

F. Disk Size

At one time 3/4-inch diameter discs were used in assay work at this laboratory. To increase recovery from low count solutions this size was increased to one inch; almost doubling the surface area of the disc. One-inch discs, however, are the maximum size which will fit the chambers of the counting machines used.

An experiment was run in which the different sized discs were directly compared. A polonium-urine sample (approximately 18 counts per minute per 50 milliliters) was acidified to 0.5 normal with hydrochloric acid, and eight two-hour runs were made, each using fifteen 3/4-inch and fifteen one-inch discs.

Statistical analysis shows no differences between the results of the various runs so that all values have been averaged into the means shown in Table XIV.

Table XIV

POLONIUM RECOVERY WITH DIFFERENT SIZED COPPER DISCS

<u>No. of Samples</u>	<u>Disc Size</u>	<u>Polonium Recovered (c./min./50 ml.)</u>
120	3/4 inch	11.47±1.57
120	1 inch	15.03±1.98

There is obviously a significantly greater recovery by the larger (one-inch) discs.

Another experiment was run in which different plating times also were used. Twelve samples of 100 milliliters (water-polonium-hydrochloric acid) were run with each disc for each plating time. Recoveries are shown in Table XV.

Table XV

POLONIUM RECOVERIES WITH DIFFERENT SIZED COPPER DISCS AND DIFFERENT PLATING TIMES

<u>Extracting Time (Hrs.)</u>	<u>Recovery (c./min./50 ml.)</u>	
	<u>One-inch Disc</u>	<u>3/4-inch Disc</u>
3	36.0	30.8
2	32.0	24.4
1.5	31.2	20.4
1	23.2	16.3
0.75	22.3	11.2

These results extend the difference shown above for two-hour platings to other plating times. All of these results are in accordance with expectations in view

of the effect which the length of plating time has on recovery and the effect, shown below, which dilution has on recovery. More plating surface can attach more polonium.

G. Polonium Recovery

1. Concentration Effect

The effect of polonium concentration in a urine solution upon the amount recovered under standard conditions is shown in the following experiment. Fifteen urine-polonium solutions were prepared at different times with counts per minute per 50 milliliters ranging from 25 to 1,128. The solutions were made 0.5 normal with hydrochloric acid and twenty aliquots were extracted for two hours with one-inch diameter discs. The results in percentage recovery shown in Table XVI were obtained.

Table XVI

POLONIUM RECOVERIES AT DIFFERENT CONCENTRATIONS

<u>Polonium Added</u> <u>(c./min./50 ml.)</u>	<u>Per Cent</u> <u>Recovered</u>	<u>Average Per Cent</u> <u>Recovered</u>
25	83.0	
	84.7	
	82.9	
	89.4	85.0
50	85.2	
	84.0	84.6
100	83.4	
	80.3	81.8
200	79.0	
	85.3	82.1
383	63.5	63.5
564	59.9	59.9
765	54.8	54.8
1,128	55.6	55.6

It is obvious from these results that above 200 counts per minute per 50 milliliters a sharp decrease in per cent recovery occurs. Other results, with water-polonium-hydrochloric acid solutions, have shown, that at varying concentrations, 90 counts per minute per 50 milliliters being the maximum, no difference in per cent recovery occurred. The decreased recovery in two-hour extractions shown above of polonium at higher concentrations might well be expected in view of the

effects which plating time and disc size have been shown to exert on recoveries. The amount of polonium plated out, according to these results, is a function of polonium concentration, time of plating, and plating-surface area.

2. Percentage Recovery Under Standard Conditions

The various data presented above show that one-inch diameter copper discs in urine solutions adjusted to an acidity of one normal with hydrochloric acid and extracted for two hours should give a good polonium recovery. These are standard conditions at present. The per cent recovery can be decreased by solutions containing over 200 counts per minute per 50 milliliters, a condition which is not usual in routine urine analysis, and might be increased by three-hour platings, though the relatively small increase probably does not justify the additional time required.

From the very large number of determinations which have been made in this research work, 313 have been performed under precisely the above conditions. The highest polonium concentration included in this group is 148 counts per minute per 50 milliliters. If the distribution of per cent recoveries among these 313 determinations is compared with a normal distribution, by means of the chi square test, it is found to be not normal. If, however, three widely discrepant per cent recoveries (27.0 per cent, 40.2 per cent, and 192.5 per cent) are discarded, the population of 310 samples is found not to differ significantly from a normal distribution. The mean per cent recovery for these 310 samples is 86.1 per cent with a standard deviation of 11.9 per cent.

Assuming, then, a normal distribution for the per cent of polonium recovery from routine urine assays, an average of 86.1 per cent of the polonium present will be recovered and counted. Sixty-seven per cent of the recoveries will fall between the values 74.2 per cent and 98.0 per cent and ninety-five per cent will fall between 62.3 per cent and 109.9 per cent.