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ANNUAL PROGRESS REPORT FOR THE
PERIOD JULY 1970—JUNE 1971

March 1972

New Brunswick Laboratory (AEC)
New Brunswick, New Jersey

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UNITED STATES ATOMIC ENERGY COMMISSION

ANNUAL PROGRESS REPORT FOR THE PERIOD
JULY 1970 THROUGH JUNE 1971

AEC Research and Development Report

Carleton D. Bingham, Director

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January 1972

NEW BRUNSWICK LABORATORY

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ABSTRACTS

High-Precision Determination of Total Uranium, Uranium(IV), and Uranium(VI) in U_3O_8 -Analyses of National Bureau of Standards 950a U_3O_8 After Ignition at Various Temperatures

The high-precision modification of the NBL titrimetric method of determining uranium has been applied to the determination of total uranium and uranium(IV) in U_3O_8 . The uranium(VI) content can also be obtained by a similar procedure. The effect of ignition temperature on the total uranium and the uranium(IV)/total uranium and uranium(VI)/total uranium ratios in NBS 950a U_3O_8 has been determined.

Automatic Instrument for the New Brunswick Laboratory Titrimetric Method of Determining Uranium - An 18-Month Evaluation

The performance of the NBL automatic uranium analyzer over an 18-month period has been evaluated. General modifications in the original instrument, maintenance problems, and the reliability as shown by analyses of control standards, are discussed.

Determination of Uranium in Uranium-Thorium Solutions by the New Brunswick Laboratory Titrimetric Method

The reliability of determining uranium in uranium-thorium mixtures (1 U:5 Th) by the NBL titrimetric method was evaluated. The relative standard deviation is 0.07% and the accuracy (relative difference) is $-0.03 \pm 0.07\%$ (95% C.L.).

Elimination of Interference of Manganese in the New Brunswick Laboratory Titrimetric Method of Determining Uranium

The interference of manganese in the NBL titrimetric method of determining uranium can be overcome by fuming the sample with sulfuric, perchloric, or phosphoric acid before the analysis.

Comparison of Prepared and Standardization Values for the Titer of Potassium Dichromate

Potassium dichromate titrant has been studied over the past several years from the standpoint of possible differences in the calculated titer (determined from the weight and purity of the dichromate in the solution) and the titer obtained by standardization with primary or secondary standards of uranium and plutonium. No significant differences have been found.

Evaluation of the Amperometric-Titration Procedure for Determining Plutonium - A Progress Report

The amperometric method of determining plutonium involving the oxidation to plutonium(VI) with argentic oxide and titration with ferrous ion was evaluated. The relative standard deviations obtained ranged from 0.07 to 0.16%. The relative errors were appreciably higher. One cause of the large errors was traced to an oxidizable impurity in the sulfuric acid diluent.

Stabilization of Ferrous Sulfate Titrant Solution - A Progress Report

Attempts were made to improve the stability of ferrous ion titrant. The most promising results were obtained by the addition of sulfamic acid to the ferrous solution.

A Brief Study on the Determination of Free Acidity in Ceric Ammonium Nitrate Solutions

The usefulness of a ceric ammonium nitrate solution to serve as a simulated plutonium(IV) solution for the determination of acidity by two different methods, iodate precipitation and citrate complexation, has been evaluated. Accurate results were not obtained with this material by either method. The citrate complexation method was found to give progressively lower results when the standing time between complexation and titration was increased.

An Evaluation of the Direct Fusion, Leach-Plus-Fusion, and Leach-Fusion Methods for the Dissolution of Plutonium Dioxide-Uranium Dioxide

Insolubles remaining after a nitric-hydrofluoric acid dissolution of mixed plutonium-uranium oxides can be treated in two ways, both of which involve a sodium bisulfate fusion. Although both are reliable, the procedure involving the evaporation of the entire solution after the acid treatment followed by a fusion is somewhat simpler and quicker than the one requiring a filtration and fusion of the separated residue.

The Effect of Humidity on Low-Fired Plutonium Oxide Samples

Some experiences with the analysis of low-fired hygroscopic plutonium oxide samples received at NBL are described. Recommendations regarding packaging of this type of material are made, and the need for an interlaboratory comparison study is pointed out.

Packaging Plutonium Metal, Alloy, and Oxide Analytical Samples for Offsite Shipment

Analyses of plutonium-aluminum alloy and plutonium oxide samples packaged either in plastic vials with snap-on caps or in sealed tubes for shipment indicated that sample integrity is best preserved in sealed tubes.

A Modified Amperometric Method of Determining Plutonium

In the amperometric determination of plutonium by oxidation with argentic oxide to plutonium(VI) followed by titration with ferrous ion, it was found that the interference of chromium, manganese, and cerium could be eliminated by reduction of the oxidized state of these elements with arsenious oxide and osmium catalyst before the final titration.

Determination of Uranium in Natural Waters by Electrical-Detection Spark-Source Mass Spectrometry

A method has been developed for the determination of uranium at concentration levels as low as $0.02 \mu\text{g./l.}$ in natural waters by spark-source mass spectrometry with electrical detection. Impurities in a water sample are incorporated into a bismuth oxide matrix and the $^{238}\text{U}/^{209}\text{Bi}$ ratio is measured with the mass spectrometer. The accuracy of the method is on the order of $\pm 5\%$.

Extension of the Refractory Carrier-Layer Method to the Determination of Other Elements in Uranium

A recently proposed spectrochemical method of determining refractories in uranium by the use of a carrier-layer technique has been extended to the determination of several other elements. The relative merits of the method are discussed.

The Spectrochemical Determination of Impurities in Aluminum-Uranium Alloys

A spectrochemical method was developed for determining impurities in aluminum-uranium alloys. By the use of a gallium fluoride-graphite buffer and complete burning of the sample, no preliminary conversion to oxide is necessary. The results obtained with samples are compared to those obtained by atomic absorption spectrophotometry.

Atomic Absorption Spectrophotometric Determination of Silicon in Boron and Boron Carbide

The existence of some uncertainty in the silicon values in boron materials obtained by emission spectrography prompted the analysis of several samples of boron and boron carbide by atomic absorption spectrophotometry as well as emission spectrography. Some differences in results were obtained.

A Tentative Gamma-Ray Spectrometric Method for the Determination of Radium-226 in Soil Samples

A tentative direct procedure for determining ^{226}Ra in soil has been developed that involves measurement of the 186-keV. gamma-ray peak. Calculations are performed by means of a FOCAL computer program.

A FOCAL Computer Program to Calculate Soil and Water Radioactivities

The determination of total alpha and beta activities plus the activities of ^{226}Ra and ^{228}Ra in soil and water samples involves corrections for background, efficiency and sample size, and, for soil samples, correction for moisture. These calculations are performed by means of a FOCAL computer program.

A FOCAL Computer Program for the Calculation of Plutonium-238/Plutonium-239 Ratios Determined by Alpha Spectrometry

A short computer program in the FOCAL language has been written to perform the necessary calculations in the determination of ^{238}Pu by alpha spectrometry. The tabular form of entry and response is used.

Evaluation of a Commercial Gravimetric Pipetter for Dispensing Control Standard Solutions

A commercially-available gravimetric titrator was evaluated for use in dispensing aliquots of standard solutions. When 10-g. or larger aliquots are dispensed, the precision and accuracy of delivery is adequate for quality control of NBL high-precision uranium and plutonium assay methods.

Calibration of the Oak Ridge National Laboratory Model Q-1348C Remote Pipetter for Hot Cell Work

The performance of the ORNL Model Q-1348C remote pipetter with 1.2-ml. capacity was evaluated. On the basis of the precision and accuracy of deliveries, the instrument appeared to be satisfactory for use at this laboratory only for dispensing aliquots between 0.5 and 1.0 ml.

HIGH-PRECISION DETERMINATION OF TOTAL URANIUM, URANIUM(IV),
AND URANIUM(VI) IN U_3O_8 -ANALYSES OF NATIONAL BUREAU OF
STANDARDS 950a U_3O_8 AFTER IGNITION AT VARIOUS TEMPERATURES

A. R. Eberle and M. W. Lerner

In a previous report,¹ the New Brunswick Laboratory (NBL) titrimetric method² for the determination of uranium involving the reduction to uranium(IV) by ferrous ion in a phosphoric acid medium, selective oxidation of the excess ferrous ion, and titration with dichromate, was applied to the precise assay of uranium metal. It was also applied,³ with slight modification, to the determination of total uranium and uranium(IV) in uranium dioxide.

In the present report, the method with some modifications was applied to the precise determination of total uranium, uranium(IV), and uranium(VI) in U_3O_8 . With the proposed methods, a study was made of the effect of ignition temperature on the assay values plus the uranium(IV)/total uranium and uranium(VI)/total uranium ratios in National Bureau of Standards (NBS) 950a U_3O_8 .

EXPERIMENTAL

Reagents and Apparatus

In addition to the reagents and apparatus listed in reference (2) Part I, the following are required:

Ferrous Ammonium Sulfate-Phosphoric Acid Solution, prepared by dissolving 30 g. of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 100 ml. of water, adding 200 ml. of 85% H_3PO_4 , and mixing.

Sulfuric Acid (1+1). After preparation, 1 ml. of 1% potassium dichromate solution is added to 200 ml. of acid solution to oxidize any reducing substances.

Potassium Dichromate Standard Solution, 0.61800 g./l. (weight corrected for buoyancy and purity), prepared from primary standard potassium dichromate, NBS 136c.

Furnace, muffle, Burrell, with Brown Electric Pyrometer and Controller unit.

Procedure

Ignition of U_3O_8 . Weigh about 13 g. of U_3O_8 into a 30-ml. platinum crucible. Place the crucible in the furnace at the desired temperature and heat for 1 hr. Remove the crucible and place in a desiccator filled with Drierite. When the U_3O_8 is cool, transfer it to a dry weighing bottle, mix it rapidly with a platinum stirring rod, cover the bottle and store it in the desiccator until used.

Determination of Total Uranium (Assay). Weigh a 2-g. sample of the oxide on a semimicrobalance (± 0.02 mg.) into a 500-ml. tall-form beaker, applying a buoyancy correction if necessary. (No corrections were made here because of the similar densities of the U_3O_8 and the weights of the Mettler balance used.) Add a mixture of 50 ml. of 85% H_3PO_4 , 1 ml. of 48% HF, and 1 ml. of the standard dichromate solution to the beaker. Heat the solution on a hot plate to near boiling. Do not allow the solution to boil. Swirl by hand and heat until the sample is dissolved completely as observed with a white background placed under the beaker. Cool the solution, wash down the beaker sides with about 50 ml. of water, and swirl to mix and dissolve any phosphate that has precipitated. Place the uncovered beaker on a steam bath overnight.

Add a sufficient quantity of freshly prepared 1M ferrous sulfate calculated to reduce the uranium(VI) portion of the sample (milliliters of ferrous sulfate solution = $4.7X$ weight of U_3O_8), measuring the solution to the nearest 0.1 ml. Swirl the solution gently and digest for 1 hr. on the steam bath. Cool to $25^\circ C$ to $26^\circ C$. Add 5 ml. of (1+1) sulfuric acid, 5 ml. of the 1.5M sulfamic acid and 2 ml. of the 1M ferrous sulfate solution. Swirl.

Place a thermometer in the solution and adjust the temperature to $35^\circ C$. Wash down the beaker sides with 10 ml. of the 8M HNO_3 -0.15M sulfamic acid-0.4% ammonium molybdate solution. Swirl the solution for a timed 2.5 min. and allow to stand for 0.5 min. Remove the thermometer, washing it with 100 ml. of water. Add a magnetic stirring bar and begin the stirring. Add a previously weighed quantity (corrected for buoyancy and purity) of solid potassium dichromate about 7.5 mg. less than that required for complete oxidation of the uranium(IV). Add 100 to 125 mg. of solid vanadyl sulfate. Insert the electrodes and titrate rapidly with the standard dichromate in a 10-ml. buret to a potential of 480 mV. Complete the titration through the end point by adding 0.10-ml. increments, reading the potential a few seconds after each addition. Calculate the volume of dichromate solution to reach the inflection point in the conventional way from the second derivative of the potentials. Add the weight of dichromate in this volume of solution to the weight of solid previously used.

Determination of Uranium(IV). Weigh a 5-g. (± 0.02 mg.) sample into a tall-form 500-ml. beaker and add 50-ml. of H_3PO_4 , 2 ml. of HF and a magnetic stirring bar. Place the beaker on a small water bath held at about $95^\circ C$ and stir the solution until the sample is dissolved (about 10 min.). Stir the solution an additional 15 to 30 min. to ensure complete dissolution. Cool the solution to $25^\circ C$.

While the solution is cooling, prepare a ferric iron solution as follows: add 5 ml. of 1M sulfamic acid solution, 5 ml. of 1M ferrous sulfate solution, and 40 ml. of H_3PO_4 to a 400-ml. beaker; wash down the beaker sides with 10 ml. of the oxidizing solution; swirl the solution until the black color disappears and then allow to stand for at least 3.0 min.

Add this ferric iron solution to the sample solution. Swirl, and allow to stand 3.0 min. Add 100 ml. of water, 100 to 125 mg.

of solid vanadyl sulfate and a quantity (the weight corrected for buoyancy and purity) of solid potassium dichromate about 7.5 mg. less than the amount required to oxidize the uranium(IV), and complete the titration as described under Determination of Total Uranium. (The weight of uranium(IV) is very close to 1/3 of the total uranium weight.)

Determination of Uranium(VI). To a weighed 2-g. (± 0.02 mg.) sample in a 500-ml. tall-form beaker, add 50 ml. of H_3PO_4 , 2 ml. of HF and a magnetic stirring bar, and dissolve as described under Determination of Uranium(IV). From the quantity of total uranium and uranium(IV), calculate the quantity of uranium(VI) in solution. Weigh a nearly equivalent amount of solid dichromate (corrected for buoyancy and purity), dissolve it in 200 ml. of 5% (v/v) H_2SO_4 , and titrate with the ferrous ammonium sulfate- H_3PO_4 solution to a potentiometric end point occurring near 680 mV. Calculate the preliminary titer of the ferrous solution.

Immediately titrate the sample solution with the ferrous solution, adding the titrant rapidly to within 0.5 ml. of the required amount. Stir the solution for 5 min. and then complete the titration with 0.10-ml. increments, waiting 2.0 min. between increments. When the potential break has been recorded (the end point potential is near 355 mV), immediately titrate another portion of dichromate as above. Use the titer obtained from this last standardization to calculate the uranium(VI) content.

RESULTS AND DISCUSSION

Determination of Total Uranium - Effect of Mixing Time During the Oxidation Step. In the general NBL titrimetric procedure,² the oxidation step requires a timed 3.0-min. period after the disappearance of the black color produced in the solution by the HNO_3 -sulfamic acid-molybdate oxidizing reagent. It was found that an error of up to +0.01% can occur in this step because of the incomplete oxidation of the excess ferrous ion when the usual 5.0 ml. quantity of ferrous solution is originally used. An error of this magnitude is not of great significance when scrap and similar samples are analyzed, but it is excessive in the highly precise and accurate determination of uranium in standard material. The error from this source can be eliminated by mixing the solution for a definite period after addition of the oxidizing reagent. (In reference [1], the quantity of ferrous ion reducing solution used for this modification is given as 5 ml. It should be 2 ml. When this smaller quantity of ferrous solution is used, i.e. when the uranium present is chiefly in the tetravalent state before the reduction step, the mixing during the oxidation step is not necessary.)

Table 1 presents the assay results on NBL dingot uranium metal (99.972% U) obtained by the proposed assay procedure with varying mixing times after the addition of the oxidizing reagent. The data indicate that a mixing time of at least 1.5 min. is required for complete oxidation of the excess ferrous ion and that no oxidation of the uranium(IV) occurs with a mixing time of up to 3.0 min.

TABLE 1

EFFECT OF MIXING TIME DURING THE OXIDATION STEP - ASSAY
OF NBL DINGOT METAL ($99.972 \pm 0.004\%$)

<u>Mixing Time, min.</u>	<u>Uranium Found, %</u>
0	99.988, 99.983
0.5	99.986, 99.986
1.0	99.979, 99.979
1.5	99.967, 99.975, 99.979
2.0	99.973, 99.973, 99.964
2.5	99.968, 99.981, 99.966
3.0	99.973, 99.975, 99.972
Average for 1.5 to 3.0 min., % = 99.972	
Relative Standard Deviation, % = 0.0052	

The experiment was repeated with NBS 950a U_3O_8 and mixing times of 1.5 to 3.0 min., Table 2. These results are much more precise than the exploratory data obtained by a 3.0 min. period with no stirring. These data also confirm the fact that a stirring period of from 1.5 to 3.0 min. is adequate for complete oxidation of the ferrous ion. The difference between the average assay value obtained and the certified value is explained under Effect of Ignition Temperature on the Assay of NBS 950a.

TABLE 2

EFFECT OF MIXING TIME DURING THE OXIDATION STEP - ASSAY
OF NBS 950a ($99.940 \pm 0.02\%$) - IGNITION AT $885^\circ C$ FOR 1
HOUR

<u>Mixing Time, min.</u>	<u>U_3O_8 Found, %</u>	<u>Average</u>
1.5	99.924, 99.931, 99.926, 99.927, 99.922, 99.927	99.926
2.0	99.924, 99.924, 99.925, 99.921, 99.922, 99.931	99.925
2.5	99.932, 99.916, 99.924, 99.927, 99.924, 99.930	99.926
3.0	99.926, 99.925, 99.924, 99.926, 99.931	99.926

Average 1.5 to 3.0 min., % = 99.926

Relative Standard Deviation, % = 0.0038

Determination of Uranium(IV) - Stability of Uranium(IV) in H_3PO_4 To determine the uranium(IV) content of U_3O_8 , the uranium-(IV) in the solution prepared from the U_3O_8 must be completely stable for the period necessary to complete the titration. Uranium(IV) has been reported to be quite stable in phosphoric acid,⁴ and brief studies³ at NBL with uranium dioxide have also indicated its stability. In the present work, additional tests were made with dingot metal.

Quantities of dingot from 3 to 3.5 g were dissolved in 50 ml. of H_3PO_4 containing either 0.5 or 2.0 ml. of HF. Dissolution temperatures were maintained at 80° to 87°C on a steam bath for 17 to 65 hr. The uranium(IV) was then determined by the proposed procedure, Table 3. The data indicate that no detectable oxidation occurs for periods of up to 18 hr., and that only small amounts are oxidized in 65 hr. The slightly high values for the 18-hr. data are attributed to a small blank in the H_3PO_4 mixture. This blank can be eliminated in the usual procedures for total uranium by pre-oxidation of the acid mixture with small amounts of dichromate, but it cannot be eliminated in the same way here because the dichromate will oxidize some uranium(IV). This blank error, then, exists in the uranium(IV) determination, and it can be as high as +0.010% absolute.

TABLE 3

STABILITY OF URANIUM(IV) AFTER DISSOLUTION OF NBL DINGOT
IN PHOSPHORIC-HYDROFLUORIC ACID

Uranium, %		Difference, %	Conditions ^a
Total Present	Uranium(IV) Found		
99.972	99.979	+ 0.007	0.05 ml HF - 17 hr
	99.978	+ 0.006	0.05 ml HF - 18 hr.
	99.962	- 0.010	0.05 ml HF - 65 hr
	99.926	- 0.046	0.05 ml HF - 65 hr
	99.983	+ 0.010	2.0 ml. HF - 18 hr.
	99.980	+ 0.008	2.0 ml. HF - 18 hr

a. All solutions contained 50 ml. H_3PO_4 maintained at 85° to 87°C, indicated time is from start of dissolution.

Determination of Uranium(VI) - Standardization of Ferrous Ion Titrant. The titration of the uranium(VI) with the ferrous ion titrant is slow because the reaction takes considerable time to reach equilibrium after each addition. To minimize the error due to instability of the titrant, the standardization made immediately after the uranium(VI) titration is used to establish the titer for the calculations. This final standardization can be made very quickly after the uranium(VI) titration and is thus more accurate than the initial standardization.

Effect of Ignition Temperature on the Assay of NBS 950a U_3O_8 .
In exploratory work with the high-precision modification of the NBL titrimetric method proposed here, it was found that somewhat low results, 99.92 to 99.93%, were invariably obtained with NBS 950a U_3O_8 , certified to be $99.94 \pm 0.02\%$ U_3O_8 . In these tests, the U_3O_8 was ignited prior to analysis for the required 1 hr. at $900^\circ C$. These results prompted a study of the effect of ignition temperature on the assay value.

In Table 4 are given the data obtained for ignition temperatures 700° to $1200^\circ C$. Some data are also given for ignition for 2 hr. at one temperature, $835^\circ C$, and for consecutive ignitions at different temperatures. All the ignitions were made with 13 g. of U_3O_8 in an open 30-ml. platinum crucible. The crucible was always placed in the identical position in the furnace. In Figure 1 the average assay values plus the relative standard deviations are plotted against ignition temperatures for the single-temperature ignitions for 1 hr.

The data listed in Table 4 and shown graphically in Figure 1 indicate that there is a linear relationship between the ignition temperature and assay value. The assay value increases by 0.008% per $100^\circ C$ temperature increase in the 700° to $1200^\circ C$ range.

Other conclusions can be drawn from the data in Table 4. It appears that the oxide assumes the assay value pertaining to the highest ignition temperature to which it is subjected. Thus, when it is ignited at $885^\circ C$, then ignited at $1035^\circ C$ and later ignited at $835^\circ C$, it will have an assay value corresponding to $1035^\circ C$. This conclusion was checked by an additional test in which a sample of the U_3O_8 was ignited at $1085^\circ C$ for 1 hr., cooled, and then re-ignited at $785^\circ C$ before analysis. The average of 6 determinations was 99.942% U_3O_8 with a relative standard deviation of 0.0036%. This value corresponds to an ignition temperature of $1080^\circ C$ according to Figure 1. This behavior may be useful in the preparation of a future standard: if it was originally ignited at $900^\circ C$ with instruction to ignite at a lower temperature to remove any moisture, the control of this lower-temperature ignition would not have to be critical.

Three other conclusions can be drawn from the data. First, the effect of ignitions for 2 hr. is identical to that for 1 hr. at the same temperature. Second, heating the material at $118^\circ C$ for 72 hr. may eliminate the moisture but it does not lead to a U_3O_8 of a definite stoichiometry as evidenced by the high value for the relative standard deviation. Third, the assay value for an ignition at $900^\circ C$ (as required by the NBS certificate) is close to 99.927% U_3O_8 rather than the certified value of 99.40% U_3O_8 . It will be noted that the temperature in Figure 1 corresponding to an assay value of 99.94% is close to $1050^\circ C$. Although it was doubtful that a $150^\circ C$ difference that would account for this discrepancy existed between the indicated and actual temperature in the furnace, this point was checked by calibrating the furnace pyrometer (indicating thermocouple).

TABLE 4

ASSAY VALUES FOR NBS 950a U_3O_8 AFTER STATED HEATING PERIODS

U ₃ O ₈ , %							
<u>118°C-72 hr.</u>	<u>700°C-1 hr.</u>	<u>785°C-1 hr.</u>	<u>835°C-1 hr.</u>	<u>835°C-2 hr.</u>	<u>885°C-1 hr.</u>	<u>935°C-1 hr.</u>	
99.821	99.914	99.924	99.918	99.920	99.924	99.928	
99.830	99.910	99.911	99.924	99.924	99.924	99.927	
99.824	99.908	99.914	99.918	99.918	99.932	99.938	
99.811	99.911	99.917	99.912	99.922	99.926	99.822	
99.823	99.909	99.919	99.925	99.924	99.931	99.925	
99.828	99.910	99.914	99.921	99.921	99.924	99.930	
99.834	99.904	99.922			99.916	99.920	
99.817	99.911	99.915			99.925	99.930	
99.831	99.909	99.922			99.926	99.931	
99.838	99.915	99.909			99.925	99.938	
		99.914			99.924	99.928	
		99.918			99.924	99.931	
					99.927	99.931	
					99.931	99.930	
					99.927	99.934	
					99.926		
					99.922		
					99.921		
					99.924		
					99.931		
					99.922		
					99.927		
					99.930		
Average, %	99.826	99.910	99.917	99.920	99.922	99.926	99.930
Relative Standard Deviation, %	0.0082	0.0031	0.0046	0.0048	0.0023	0.0038	0.0050

TABLE 4 (Continued)

ASSAY VALUES FOR NBS 950a U_3O_8 AFTER STATED HEATING PERIODS

U_3O_8 , %				
	885°C-1 hr.,			
	985°C-1 hr.	1035°C-16 hr., 835°C-1 hr.	1085°C-1 hr.	1185°C-1 hr.
	99.932	99.933	99.940	99.953
	99.936	99.942	99.943	99.947
	99.936	99.943	99.940	99.958
	99.939	99.940	99.945	99.945
	99.929	99.937	99.940	99.949
	99.941	99.935	99.941	99.953
	99.939		99.940	
	99.926		99.941	
	99.933		99.944	
	99.934		99.943	
	99.927		99.947	
Average, %	99.934	99.938	99.942	99.951
Relative Standard Deviation, %	0.0050	0.0040	0.0024	0.0048

FIGURE 1. EFFECT OF IGNITION TEMPERATURE
ON THE ASSAY OF NBS-950a U_3O_8 .

Calibration of Furnace Pyrometer. The pyrometer was first checked against a second chromel/alumel thermocouple. This test showed that the pyrometer was indicating to within 20°C of the test thermocouple. A calibration was then made by placing clear Vycor crucibles at the actual sample placement sites and determining in these crucibles the melting points of sodium chloride, silver wire, and gold wire. These data, shown in Table 5, indicate that the actual temperatures of ignition were about 15°C cooler than those indicated by the pyrometer. The temperatures referred to in this report are the corrected temperatures.

TABLE 5
CALIBRATION OF FURNACE PYROMETER WITH
MELTING POINT STANDARDS

Melting Point Standard	Melting Point, °C	Controller Setting, °C	Indicated Temperature Range, °C	Physical State of Standard	Temperature Difference, °C
Sodium chloride	801	800	790-810	solid	
		810	805-822	liquid	
		Average of high points, °C = 816			+ 15
Silver	961	960	955-972	solid	
		970	965-980	liquid	
		Average of high points, °C = 976			+ 15
Gold	1063	1060	1050-1070	solid	
		1070	1065-1085	liquid	
		Average of high points, °C 1077.5			+ 14.5

Assay of U₃O₈ Prepared from Dingot Metal. To assess the reliability of the proposed U₃O₈ assay procedure, NBL dingot metal, on which the assay values summarized in reference (1) have been obtained by several laboratories including NBL,¹ was converted to U₃O₈. The conversion consisted of igniting an accurately weighed 12-g. sample of the dingot in a 15-ml. tared platinum dish at 700°C for 65 hr. and then at 900°C for 1 hr. The resulting oxide was weighed and calculated to be 99.928% U₃O₈ on the basis of the weight change. (The weight loss of the platinum dish was determined and was found to have no effect on the final result.)

Samples of the oxide of about 2-g. each were then assayed by the proposed procedure. The data are shown in Table 6. The average value of 7 determinations was 99.927% U₃O₈ and this value can be compared to the 99.928% found above. The excellent agreement indicates that the proposed assay procedure is extremely reliable.

Effect of Ignition Temperatures on Uranium(IV) and Uranium(VI) Content of U₃O₈. It was of interest to determine how the ignition temperature affected the uranium(IV) and uranium(VI) content of U₃O₈. This study would also be of value in assessing the reliability of determining the uranium(IV) and the uranium(VI).

TABLE 6
ASSAY OF U_3O_8 PREPARED FROM NBL DINGOT URANIUM METAL

	Found, %	
	As Uranium	As U_3O_8
	84.741	99.930
	84.738	99.927
	84.740	99.929
	84.739	99.928
	84.734	99.922
	84.736	99.924
	<u>84.743</u>	<u>99.932</u>
Average, %	84.739	99.927
Relative Standard Deviation, %	0.0036	0.0035
(Ignition Value, %	84.739	99.928)

The data in Table 7 were obtained by igniting NBS 950a U_3O_8 at various temperatures for 1 hr. and then analyzing the material for both uranium(IV) and total uranium. The results are expressed as the ratio of uranium(IV)/total uranium. Unexpectedly, the ratio is seen to increase with increasing temperature. It is important to note that the theoretical ratio 0.33333 is reached at a temperature a few degrees below $900^{\circ}C$, but at this temperature the material, according to Table 4, is not 100% U_3O_8 but 99.926%. Since the total impurities of the U_3O_8 are about 50 ppm. they alone cannot account for the value of 99.926% U_3O_8 . The material, then, at this temperature is not $UO_2 \cdot 2UO_3$ but $UO_{2+x} \cdot 2UO_{3+x}$.

TABLE 7
EFFECT OF IGNITION TEMPERATURES ON URANIUM(IV)/TOTAL URANIUM RATIOS IN NBS 950a U_3O_8
Uranium(IV)/Total Uranium Ratio

	Ignition Temperatures ^a					
	($118^{\circ}C$)	$700^{\circ}C$	$800^{\circ}C$	$900^{\circ}C$	$985^{\circ}C$	$1185^{\circ}C$
	0.32873	0.33167	0.33258	0.33345	0.33361	0.33491
	0.32872	0.33172	0.33230	0.33359	0.33365	0.33473
	0.32863	0.33176	0.33238	0.33343	0.33356	0.33489
	0.32832	0.33177	0.33240	0.33351	0.33369	0.33489
	0.32866				0.33371	
	<u>0.32857</u>					
Av.	0.32860	0.33173	0.33242	0.33350	0.33364	0.33485

a. All material dried first at $118^{\circ}C$ for 72 hr.

The uranium(VI)/total uranium ratios are shown in Table 8 for two ignition temperatures. They confirm the data in Table 7 in that now as the temperature rises the uranium(VI) drops. In Table 8 the uranium(VI)/total uranium ratios calculated by difference from the uranium(IV) values are also given. The determined and the calculated ratios agree to within 0.04%. It is felt that the ratios calculated by difference are probably more accurate because the two determinations used, even considering the blank error of the uranium(IV) determination, are very reliable, whereas the uranium(VI) determination that involves a poor end point and an unstable titrant is less so.

TABLE 8
EFFECT OF IGNITION TEMPERATURES ON URANIUM(VI)/TOTAL
URANIUM RATIOS IN NBS 950a U_3O_8

	Uranium(VI)/Total Uranium Ratio		
	Ignition Temperatures ^a		
	(118°C)	985°C	1185°C
	0.67186	0.66671	0.66490
	0.67102	0.66662	0.66574
	0.67137	0.66620	0.66544
	0.67199	0.66649	0.66521
	0.67178	0.66644	0.66545
		0.66631	0.66644
			0.66403
			0.66588
Average	0.67160	0.66646	0.66539
Calculated by Difference	0.67140	0.66636	0.66515
Relative Difference, %	+0.030	+0.015	+0.036

a. All material dried first at 118°C for 72 hr.

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4. American Standards Association Report ASA N5.7, (1965), p. 23.

AUTOMATIC INSTRUMENT FOR THE NEW BRUNSWICK LABORATORY
TITRIMETRIC METHOD OF DETERMINING URANIUM —
AN 18-MONTH EVALUATION

M. R. Clickner, C. G. Goldbeck, and M. W. Lerner

The automatic instrument¹ for the determination of uranium by the New Brunswick Laboratory (NBL) titrimetric method involving the reduction to uranium(IV) by ferrous ion in phosphoric acid, selective oxidation of the excess ferrous ion, and titration with dichromate, has been in nearly continuous use for 18 months. In the present report, its performance to date is evaluated, some modifications to the instrument are described, and maintenance problems are noted. A summary of the results obtained for a group of control standards analyzed routinely with each group of samples is also presented.

Modifications Made in Instrument

The calomel reference electrode proved to be one source of difficulty under prolonged use of the instrument. The commercial-type electrode frequently gave a poor end-point response, in some cases because of build-up of salts above the fiber contact. The substitution of a silver-silver chloride reference electrode, used occasionally in the original developmental work, proved to be advantageous. The electrode was constructed as before by fitting a 1/4-in. O.D. by 1/2-in. long piece of Vycor rod into a short length of tygon tubing fitted on the end of a glass tube. This electrode works satisfactorily if the saturated potassium chloride solution containing the silver chloride is replaced frequently. However, if this precaution is not taken, contamination of the electrode by slow leakage past the Vycor rod occurs, and low results due to an improper reference potential are obtained.

Another change proposed in the original report,¹ the substitution of an electronic timer-programmer for the mechanical cam-type unit, was made during this time. The new timer, an Agastat Programmer Model 2912 made by Amerace-Esna Corporation, provides for 12 steps per cycle, with dwell times per step of 0.25 sec. to 10 min. controlled by a calibration dial for each step. This timer controls the timing of the reagent addition much more precisely than the original timer and, in addition, resets for the next cycle immediately after the completion of a titration. This latter feature saves from 1- to 4- min. time on nearly every sample. One change made in the programming with the new timer was the starting of the stirring only after the addition of the sulfamic acid and ferrous ion- H_3PO_4 reagents, rather than before any reagent addition. With the new program, the stirrer paddles are covered with solution when the stirring starts and less splattering occurs. Another change that was made involves the use of the cut-off switch incorporated in the turn-table. It is being used to

stop the operation after the last sample is titrated, and the instrument can now be loaded with fresh samples at the end of a working day to increase the daily output by as much as 12 samples.

The new timer has one other advantage. Previously, when the capacity of the buret was reached in the titration of a sample made unknowingly too large, the turn-table would not present a fresh sample, yet a new cycle of reagent addition into the same beaker would begin. The beaker would overflow, and if no attention was given the instrument, this type of recycling would occur again and again. With the new timer, the cycle simply stops when the buret is empty, and nothing more happens until the instrument is re-started manually.

Occasionally, after delivery of the ferrous ion- H_3PO_4 reagent, the last drop would not be knocked off the delivery tube tip by the momentary squeezing of the tube by the solenoid. This drop then would sometimes fall into the solution during titration and cause high results. It was found that the substitution of a polyethylene tip for the glass tip coated with a non-wetting agent reduced materially the frequency of this source of error.

The time needed to pump both the ferrous ion- H_3PO_4 reagent and the diluent was cut in half by equipping the peristaltic pumps with "piggy-back" heads designed to double the pumping rate. This step has saved nearly 1 min. for each analysis.

Finally, two minor changes were made to improve the "seeking" action as the end point is approached. First, the thin gold wire indicator electrode was replaced by a stouter wire (14 gage) to prevent the shifting of that portion, held in the electrode cup and exposed to the titrant flow, away from its optimum position between runs. Second, it was found that excessive "seeking" was caused not only by the titrant delivery tip being too close to the gold electrode in the cup, but also by inefficient stirring. Consequently, the disk stirrer, which has been used to lessen splatter since the issuance of the report in reference (1), was replaced by the paddle stirrer originally described and the stirring speed as a result increased.

Instrumental Maintenance. Considering the time the instrument has been in nearly continuous use during the past 18 months, the maintenance problems have been minimal. The stirrer and syringe drive motors needed replacement after about 12 months. The matched electrometer tubes that control the zero point setting were replaced to eliminate drifting of the potential. After about 14 months the instrument appeared to respond sluggishly e.g. progressively higher titrations were obtained with identical standards over a period of time. Replacement of the printed circuit boards corrected this difficulty. Finally, the plastic syringe body assembly was replaced because of failure of the threaded portion.

Precision and Accuracy of Control Standards. In the period of 7/28/71 to 8/4/71, there were 59 determinations made by the titrator on four different standard uranium solutions made at different times by two people. The standard solutions were prepared from NBL dingot uranium metal (99.972% uranium), and the

concentrations ranged from 0.017142 to 0.013704 g. uranium/g solution. The relative standard deviation of these results was 0.06% and the relative difference from the prepared value was $+0.009 \pm 0.016$ (95% C.L.), the latter values indicating the absence of bias.

REFERENCE

1. Goldbeck, C. G., Lerner, M. W., and Rodden, C. J., NBL-252, Part II, (June 1970), p. 26

DETERMINATION OF URANIUM IN URANIUM-THORIUM SOLUTIONS
BY THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD

A. R. Eberle and M. W. Lerner

The New Brunswick Laboratory (NBL) titrimetric method¹ of determining uranium involving the ferrous ion reduction in phosphoric acid, selective oxidation of the excess ferrous ion with nitric acid-molybdate, and titration of the uranium(IV) with dichromate, has been applied to a wide variety of sample types. Precisions and accuracies have been reported of the analyses of mixtures of uranium with large quantities of aluminum, aluminum-niobium, aluminum-zircaloy, stainless steel elements, and plutonium. In the present brief report, the reliability of the analysis of uranium-thorium solution is presented.

EXPERIMENTAL

The reagents, apparatus, and procedure are identical to those described in reference (1), Part I for the potentiometric titration.

RESULTS

Seven replicate analyses were made of a standard uranium solution containing 100 mg. of uranium and 0.5 g. of thorium. The solution contained 10% HNO₃ and about 0.3% H₂SO₄. The results are shown in Table 1.

TABLE 1

REPLICATE ANALYSES OF A STANDARD URANIUM-THORIUM SOLUTION

Uranium, mg.		Remarks
Present	Found	
100.81	100.81	Evaporated dry; 10 ml. water added
100.21	100.17	" " "
100.63	100.65	" " "
100.79	100.78	" " "
100.42	100.30	" " "
101.14	101.20	Fumed with 5 ml. HClO ₄ ; 10 ml. water added
100.65	100.52	Fumed with 10 ml. HClO ₄ ; 10 ml. water added

Relative Standard Deviation = 0.07%

Accuracy (relative difference) = $-0.03 \pm 0.07\%$ (95% C.L.)

REFERENCE

1. Eberle, A. R., Lerner, M. W., Goldbeck, C. G., and Rodden, C.J., NBL-252, Part I (July 1970).

ELIMINATION OF INTERFERENCE OF MANGANESE IN THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD OF DETERMINING URANIUM

A. R. Eberle and M. W. Lerner

In a previous report,¹ manganese was stated to give small negative errors in the New Brunswick Laboratory (NBL) titrimetric method of determining uranium. In this method involving the reduction of uranium(IV) by ferrous ion in phosphoric acid and titration with dichromate or by constant current coulometry,² it was postulated that manganese is oxidized to a valence state in which it is capable of oxidizing uranium(IV), thereby causing low results to be obtained. In the present work a study was made of this interference. Although the mechanism of the interference is still unknown, means have been found to overcome the effect of up to 25 mg. of manganese, a quantity much higher than would be normally present in the usual sample size of 100 to 250 mg. of uranium.

EXPERIMENTAL

Reagents and Apparatus

Standard Uranium Solution, prepared on a weight basis by dissolving NBL dingot uranium metal in HNO_3 plus a small amount of H_2SO_4 and diluting with water.

Manganous Sulfate Solution, 5 mg. Mn/ml.

All other reagents and apparatus are identical to those given in reference (1), Part I.

Procedure

Titrate the uranium by the basic procedure described in reference (1), Part I.

RESULTS AND DISCUSSION

Elimination of Interferences of Manganese. Two series of uranium determinations were made on sample solutions containing about 120 mg. of uranium and from 0 to 25 mg. of manganese to obtain additional information regarding the extent of the interference, Table 1. In these tests, the appropriate weight of standard uranium solution plus the manganese spike was evaporated to dryness on a steam bath and the salts were taken up in 10 ml. of water for the analyses. The data confirm the interference of manganese and the fact that the extent of the interference does not depend strictly on the manganese concentration.

TABLE 1

ANALYSIS OF URANIUM SOLUTIONS CONTAINING MANGANESE AFTER
EVAPORATION TO DRYNESS AND DISSOLVING SALTS IN WATER

<u>Manganese Present, mg.</u>	<u>Relative Error (Difference),^a %</u>	
	<u>Series No. 1</u>	<u>Series No. 2</u>
0	+0.03	+0.05
0	-	0.00
2	-0.12	-0.03
5	-0.14	-0.16
10	-0.26	-
15	-0.19	-0.28
25	-0.25	-0.26

a. 120 mg. U present

Two similar series of determinations were then made on solutions prepared as above with the exception that the salts were taken up in 10 ml. of 10% HNO_3 before the analyses, Table 2. These data again show some negative errors with large amounts of manganese but in most cases the effect is apparently less than is shown by the data in Table 1. The absolute concentration of nitrate then, does not appear to be the chief factor in the interference.

TABLE 2

ANALYSIS OF URANIUM SOLUTIONS CONTAINING MANGANESE AFTER
EVAPORATION TO DRYNESS AND DISSOLVING SALTS IN
10% NITRIC ACID

<u>Manganese Present, mg.</u>	<u>Relative Error (Difference),^a %</u>	
	<u>Series No. 1</u>	<u>Series No. 2</u>
0	+0.03	-0.01
0	-0.08	-0.08
2	-0.02	-0.04
5	-0.09	-0.04
10	-0.12	-0.11
15	-0.12	-0.10
25	-0.09	-0.28, -0.20

a. 120 mg. U present

Similar analyses were made after fuming the solutions with H_2SO_4 , HClO_4 , or H_3PO_4 . In the H_3PO_4 tests, the usual 40 ml of H_3PO_4 was used for the fuming step, the solution was then diluted with 25 ml of water and boiled before the analyses. The data are shown in Table 3. It can be seen that the fuming step is effective in eliminating the interference of manganese. Apparently in the complete absence of nitrate in the sample the manganese does not interfere. Note that the elimination of the interference by fuming with H_2SO_4 is somewhat more effective than by fuming with HClO_4 . This relative behavior parallels the known effectiveness of these acids in eliminating nitrate by fuming.

TABLE 3

ANALYSIS OF URANIUM SOLUTIONS CONTAINING MANGANESE AFTER FUMING WITH VARIOUS ACIDS AND DILUTING WITH WATER

Manganese Present, mg.	Relative Error (Difference), ^a %		
	H_2SO_4 (5 ml.)	HClO_4 (5 ml.)	H_3PO_4 (40 ml.)
0	+0.06	0.00	-
0	+0.03	+0.08	+0.06
2	+0.08	-0.05	+0.05
5	-0.09	-0.13	+0.08
10	+0.10	-0.09	-0.03
15	-0.02	-0.16	-0.08
25	-0.02	-0.08	-0.13

a. 120 mg. U present

Oxidation State of Manganese in the NBL Titrimetric Method
Manganous ion is readily oxidized in strong H_3PO_4 medium by chromate or dichromate and, to a lesser extent, by HNO_3 or HClO_4 to a purple product.³ The color resembles the permanganate color but is, in reality, due to Mn(III) . The reaction may be expressed as

It has been shown⁴ that the purple manganese product is an anion $[\text{Mn}(\text{PO}_4)_2]^{-3}$. The overall reaction, then, can be written

In the present work, it was confirmed that the oxidation of Mn^{+2} to Mn^{+3} by dichromate can occur in H_3PO_4 medium. It was shown spectrophotometrically that the reaction goes to completion and that the absorbance of the Mn^{+3} is only 1/20 of that for the

same quantity of permanganate. Beer's Law holds in the range of 2 to 25 mg. manganese per 50 ml. of solution.

This reaction can only occur in strong H_3PO_4 medium; it cannot proceed in the diluted solution of the NBL titrimetric method immediately before the titration step. On the other hand, oxidation of the Mn^{+2} can also occur with HNO_3 in strong H_3PO_4 medium, although heating is apparently necessary for quantitative reaction.³ Therefore, some oxidation of Mn^{+2} to Mn^{+3} possibly occurs during the oxidation step of the NBL procedure. If oxidation at this point is the source of the manganese interference, however, it is difficult to understand why the fuming steps described above eliminate the interference.

Samples received at NBL for uranium analyses frequently contain nitrates or free nitric acid. It is customary to fume all solutions of unknown composition down with H_2SO_4 , HClO_4 , or H_3PO_4 prior to the analyses. If H_2SO_4 or H_3PO_4 are used, at least 25 mg. of manganese will give no interference; if HClO_4 is used, a smaller amount, perhaps 2 mg., can be positively tolerated. If the analyst is concerned about the presence of manganese in the sample aliquot to be analyzed, the addition of a few drops of dichromate solution to the solution after the addition of the H_3PO_4 will reveal its presence by the formation of the purple color of Mn^{+3} . Down to 2-mg. quantities are easily detected by this test.

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COMPARISON OF PREPARED AND STANDARDIZATION VALUES FOR THE TITER OF POTASSIUM DICHROMATE

C. E. Pietri, A. W. Wenzel, and H. N. Simmons

National Bureau of Standards (NBS) primary oxidimetric standard potassium dichromate is used at the New Brunswick Laboratory (NBL) in the titrimetric determination of plutonium and uranium. The standard solutions of dichromate after preparation are routinely checked against standards of plutonium and/or uranium to ensure that the prepared value is correct. The present report compares the results obtained over a period of several years for the calculated titers of randomly-selected lots of dichromate solutions and the corresponding values obtained by standardization.

EXPERIMENTAL

Reagents and Apparatus

Potassium Dichromate, NBS No. 136a and 136b.

Plutonium Sulfate Tetrahydrate, NBS No. 944.

Plutonium Metal, NBS No. 949a and 949b.

Uranium Oxide, U_3O_8 NBS No. 950a.

Uranium Metal, NBL dingot.

Uranium-Plutonium Nitrate, prepared from plutonium sulfate tetrahydrate NBS No. 944 and U_3O_8 NBS No. 950a.

Plutonium Nitrate and Plutonium-Aluminum Nitrate, analyzed solutions prepared from process samples.

The other reagents and the apparatus have been described in previous reports in which the analytical procedures are described.^{1-3,5}

Procedure

Standardize the dichromate solutions, prepared to a known titer on the basis of the weight and purity of potassium dichromate and the weight of the final diluted solution, against uranium and/or plutonium standards and compare the prepared value with this value. Use the plutonium analytical procedure described in references (1) and (2), and the uranium procedure described in reference (4).

RESULTS AND DISCUSSION

From the historical record of 88 lots of dichromate titrant prepared over the past several years, 15 lots were selected at random for examination. From the data shown in Table 1, three conclusions can be drawn. One, there is invariably no detectable difference between the calculated titer based upon the weight and purity of dichromate and the final weight of titrant solution, and the titer found by standardization with a primary standard uranium or plutonium or secondary standards calibrated from them. The calculated titer, therefore, can be used although it is not recommended, without confirmation by standardization. Two, there is no difference between standardization with plutonium and uranium standards. Three, both the standards and methods used for standardization are reliable and will readily detect any error in the preparation of the standard dichromate.

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5. Pietri, C. E., Anal. Chem., 34, 1604 (1962).

TABLE 1

RELATIVE DIFFERENCE OF STANDARDIZED VALUES FROM THE PREPARED VALUE
OF POTASSIUM DICHROMATE STANDARD SOLUTIONS

<u>K₂Cr₂O₇</u> <u>Lot No.</u>	Relative Difference, %						
	NBS Standards			NBL Standards			
	No. 944 <u>Pu(SO₄)₂·4H₂O</u>	No. 949a, b <u>Pu Metal</u>	No. 950a <u>U₃O₈</u>	<u>U Metal</u>	<u>Pu(NO₃)₄</u>	<u>(U-Pu)NO₃</u>	<u>(Pu-Al)NO₃</u>
1	-0.01 -0.04 -0.05	-0.03 +0.04					
2	0.0 +0.02 +0.04	+0.02 +0.04					
3	0.0 +0.05 +0.01	-0.03 +0.06 +0.05					
4	-0.05, +0.01 +0.03, +0.05 -0.01, 0.0 0.0	+0.01 +0.02 +0.05		-0.07 +0.08 +0.04 +0.02			
5	0.0 +0.05 +0.02		-0.04 -0.08 +0.03 +0.03	+0.07 +0.09 +0.02 +0.02			
6	+0.02 +0.03			-0.04 +0.05 +0.03			
7	+0.02 -0.08 +0.02 -0.03			+0.07 -0.01 -0.03			

TABLE 1 (Continued)

RELATIVE DIFFERENCE OF STANDARDIZED VALUES FROM THE PREPARED VALUE
OF POTASSIUM DICHROMATE STANDARD SOLUTIONS

$K_2Cr_2O_7$ Lot No.	Relative Difference, %						
	NBS Standards			NBL Standards			
	No. 944 $Pu(SO_4)_2 \cdot 4H_2O$	No. 949a, b <u>Pu Metal</u>	No. 950a <u>U_3O_8</u>	<u>U Metal</u>	<u>$Pu(NO_3)_4$</u>	<u>$(U-Pu)NO_3$</u>	<u>$(Pu-Al)NO_3$</u>
8	-0.03		+0.08		0.0		
	-0.02		+0.08		-0.05		
			-0.02		-0.04		
			+0.03		+0.03		
9				+0.04		+0.05	
				+0.05		-0.06	
				-0.09		+0.03	
				0.0		+0.04	
				-0.02			
10				+0.01	+0.01		
				+0.07	-0.07		
				-0.05			
11				+0.07, -0.07	-0.07		
				-0.06, -0.02	-0.07		
				-0.06, +0.02	+0.04		
				+0.02, +0.03	+0.01		
12				+0.10			-0.05
				-0.05			-0.02
				+0.04			-0.04
				+0.02			+0.02
13	-0.03			+0.07			-0.07
				+0.09			-0.05
				-0.02			+0.03

TABLE 1 (Continued)

RELATIVE DIFFERENCE OF STANDARDIZED VALUES FROM THE PREPARED VALUE
OF POTASSIUM DICHROMATE STANDARD SOLUTIONS

$K_2Cr_2O_7$ Lot No.	Relative Difference, %						
	NBS Standards			NBL Standards			
	No. 944 <u>$Pu(SO_4)_2 \cdot 4H_2O$</u>	No. 949a, b <u>Pu Metal</u>	No. 950a <u>U_3O_8</u>	<u>U Metal</u>	<u>$Pu(NO_3)_4$</u>	<u>$(U-Pu)NO_3$</u>	<u>$(Pu-Al)NO_3$</u>
14				+0.03, -0.07 +0.02, +0.02 -0.01, +0.02		+0.05 +0.02 -0.06	
15				-0.02 +0.05 +0.04		-0.07 -0.02 +0.03	

EVALUATION OF THE AMPEROMETRIC-TITRATION PROCEDURE FOR DETERMINING PLUTONIUM — A PROGRESS REPORT

K. Lewis

Continuing the evaluation¹ of existing methods for the determination of plutonium, the amperometric procedure was next investigated. This amperometric-titration procedure would be a useful technique at the New Brunswick Laboratory (NBL) because it is a high-precision procedure that only requires 10 to 20 mg. of plutonium. The currently-used high-precision NBL method² involving reduction with a Jones reductor and titration with potassium dichromate to a constant-current potentiometric end point requires 100 to 200 mg. of plutonium.

The amperometric procedure^{3,4} consists of oxidation of plutonium to Pu(VI) with argentic oxide, destruction of the excess Ag(II), and titration with a standard ferrous ion solution. The end point is detected amperometrically at a rotating platinum electrode which is polarized to a potential at which it responds linearly to the presence of ferrous ion.

EXPERIMENTAL

Reagents and Apparatus

Argentio Oxide, prepared at NBL by the persulfate oxidation of Ag(I).⁵

Ferrous Ammonium Sulfate Titrant, 0.05N in 1N H₂SO₄.

Potassium Dichromate Solution, prepared by weight from primary standard potassium dichromate.

Amperometric Titrator, E. H. Sargent and Company, Ampot S-29710 modified for use with an external picoammeter, with S-30420 platinum electrode and S-76485 electrode rotator.

Picoammeter, Keithley Instruments Model 414A.

Reference Electrode, a mercury-mercurous sulfate, saturated potassium sulfate electrode.

Cell, 50-ml. pyrex beaker.

Weight Buret,⁴ 1-oz. polyethylene bottle with elongated tip.

Procedure⁴

Standardization of Ferrous Titrant. To a 50-ml. beaker transfer from a weight buret a quantity of standard dichromate solution containing 5 to 10 mg. of potassium dichromate and dilute with 25

ml. of 6N H_2SO_4 . Insert the platinum and reference electrodes and start the platinum electrode rotation. Polarize the platinum electrode at 0.6 v. vs. the reference electrode. Add increments of the ferrous solution in a weight buret to the dichromate solution until a steady current of 1 to 2 μA is observed. Record the current and weight of ferrous solution used. Add sufficient ferrous solution to obtain a current of 15 to 20 μA and again record the current and weight of solution used. Calculate the titer as given below.

Analysis of Samples Deliver a weighed portion of the sample solution containing 10 to 20 mg. of plutonium to a 50-ml beaker using 0.5M H_2SO_4 as a wash solution if necessary. Add 3 to 5 drops of H_2SO_4 and fume the solution to dryness under a heat lamp. Dissolve the cooled residue in 10 ml of 0.5N H_2SO_4 . Add 25-mg portions of argentic oxide until an excess is noted by the presence of a blackish-brown color and/or a black precipitate. After 10 min add 2 ml. of saturated sulfamic acid solution and stir until the solution is clear. Wash down the beaker sides with 25 ml of 6N H_2SO_4 . Insert the electrodes and titrate as above. Calculate the plutonium quantity as given below.

Calculations. For the standardization of the titrant, determine the slope in $\mu\text{A/g.}$ of the excess ferrous ion portion of the curve by dividing the difference between the two current readings by the difference of the corresponding weights of titrant. Divide the first current reading by this slope to determine the quantity of excess ferrous solution used, then subtract this quantity from the first weight of titrant to obtain the quantity of ferrous solution needed to reach the end point. Finally, divide this value into the quantity of dichromate taken in milliequivalents to obtain the titer in meq/g titrant.

For the analysis of samples, determine the quantity of ferrous solution needed to reach the end point as given above and multiply this value by the titer and by the equivalent weight of plutonium (Calculate the equivalent weight of the plutonium from the appropriate isotopic composition.)

RESULTS AND DISCUSSION

A number of series of plutonium determinations were carried out to determine the precision of the procedure, Table 1. The relative standard deviations (RSD) obtained ranged from 0.07 to 0.16%. These values are somewhat higher than the 0.03 to 0.05% reported by Larsen, Seils, and Meyer.^{3,4} They do agree closely, however, with the precision data obtained by two laboratories evaluating the procedure as given in reference (6). This level of precision was considered to be unsatisfactory and not well understood since the precision of the standardization step was consistently about 0.05% (RSD) or below.

The relative errors shown in Table 1 vary over a wide range. Since the solutions used for these studies were prepared from old, stored plutonium standard materials, some doubt existed in regard to their known values. The accuracy, therefore, had to be evaluated by further work. These additional studies, as described below,

indicated that the standardization titration was the cause of most of the error.

TABLE 1

PRECISION OF AMPEROMETRIC PLUTONIUM DETERMINATION

Sample	Number of Aliquots	mg. Pu/g. Solution		Relative Standard Deviation, %	(Relative Error, %)
		Taken	Found		
S-22-25	8	7.970	7.956	0.16	- 0.18
S-22-29	5	3.802	3.792	0.11	- 0.26
S-22-30	4	3.827	3.827	0.08	0.0
S-28-3	6	3.596	3.606	0.12	+ 0.28
IE	4	6.866	6.878	0.07	+ 0.18

Plutonium sulfate solutions analyzed by the routine NBL constant current potentiometric procedure were also analyzed by the amperometric procedure. These plutonium solutions were prepared by WADCO from plutonium sulfate tetrahydrate isotopic standards. Before this comparison was carried out, however, the two potassium dichromate standard solutions used for each procedure were compared to one another by amperometric titration against the same ferrous solution. The results of these titrations indicated that a discrepancy existed between the two solutions, Table 2.

TABLE 2

AMPEROMETRIC TITRATION OF TWO DICHROMATE SOLUTIONS

<u>K₂Cr₂O₇ Solution</u>	<u>K₂Cr₂O₇, mg./g. Fe(II) Solution</u>
No. 61 (Amperometric)	2.3205
No. 78 (Potentiometric)	2.3262

Dichromate solution No. 78 had been recently prepared and standardized against both uranium and plutonium standards, whereas solution No. 61 had been stored for several months. Therefore, it was assumed that the standardization of solution No. 78 was correct and this solution was used in the amperometric determination of the standard plutonium sulfate solutions.

The results of the comparison tests are shown in Table 3.

TABLE 3
COMPARISON OF AMPEROMETRIC AND POTENTIOMETRIC
RESULTS ON PLUTONIUM SOLUTIONS

Pu Solution	Pu, %			Relative Difference after Am Correction, %
	Potential- metric	Ampero- metric	Relative Difference, %	
A Dresden	47.45	47.57	- 0.25	+ 0.16
C Dresden	47.46	47.61	- 0.32	+ 0.23
I Yankee	47.35	47.47	+ 0.25	+ 0.16

One difficulty arises when the data in Table 3 are compared. The plutonium sulfate standard solutions contained americium, (0.12% and 0.18% for the Dresden and Yankee material, respectively). Americium does not interfere with the NBL potentiometric procedure. However, studies carried out at Los Alamos⁷ showed that americium interferes with the amperometric procedure but its effect is neither quantitative nor strictly proportional to the americium concentration. Based upon the data in the Los Alamos report, the correction for the americium contents here can be estimated to be about -0.09% for both samples. When this correction is applied to the data, the last column in Table 3 is obtained. Thus, it would appear that the amperometric results are still high, and the possibility exists of an error in the standardization.

Standardization titrations to obtain the value of mg $K_2Cr_2O_7$ /g. ferrous solution were carried out under varying conditions. First, amperometric and potentiometric titrations with the same solutions were carried out. The amperometric titrations gave a higher value for the titer of the ferrous solution. In the potentiometric titration, the ferrous ion is titrated with dichromate, whereas in the usual amperometric titration, the titrant is the ferrous ion, although the reverse titration can be carried out satisfactorily. Therefore, the amperometric titration was performed both ways, and again a difference nearly identical to the difference between the amperometric and potentiometric titration was obtained. These facts could be explained by assuming the presence of an oxidizable impurity in the acid used to dilute the dichromate or ferrous ion prior to titration. Accordingly, amperometric titrations were next carried out with ferrous titrant and treating either the diluting acid or the diluted dichromate solution with argentic oxide and sulfamic acid prior to the titration. The results of two series of titrations are shown in Table 4.

Thus, treatment with argentic oxide changes the value of the titer to about the same extent as that obtained in the reverse direction. This oxidizable impurity in the acid is apparently capable of being oxidized by a large excess of dichromate as would occur when the dichromate aliquot is diluted with acid and titrated with ferrous ion, but cannot be oxidized by only a momentary trace of excess as would occur during the titration of the diluted ferrous with dichromate. Under the conditions of the usual titration,

condition 1 in Table 4, this impurity causes a high ratio to be obtained and the final plutonium result is accordingly high also.

The work is continuing.

TABLE 4
COMPARISON OF AMPEROMETRIC STANDARDIZATION

Titration Conditions	g. $K_2Cr_2O_7$ Solution/g. Ferrous Solution	
	Series 1	Series 2
1. Direct, Fe(II) titrant	0.6386	0.6619
2. Direct, $K_2Cr_2O_7$ titrant	--	0.6610
3. Fe(II) titrant, diluted $K_2Cr_2O_7$ treated with AgO	0.6378	0.6608
4. Fe(II) titrant, diluting acid treated with AgO	0.6380	0.6611

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STABILIZATION OF FERROUS SULFATE TITRANT SOLUTION - A PROGRESS REPORT

C. E. Hedrick

A disadvantage of the use of ferrous ion titrant is its instability. Slow air oxidation of the ferrous ion makes frequent standardizations necessary for precise work. The present work was undertaken to improve the stability without sacrificing reducing power or resorting to special storage arrangements.

The preparation recommended by Kolthoff and Belcher¹ involves the use of ferrous ammonium sulfate hexahydrate in 0.5 to 1N H_2SO_4 . The double salt apparently is preferred for reasons other than stability, but the dilute H_2SO_4 medium may increase the stability of the solution to a degree.^{2,3} Neutralization of any acid in ferrous solutions increases the air oxidation rate.⁴ Platinum black, nitric oxide, and activated carbon also accelerate the rate of decay of ferrous solutions exposed to air.⁵ A peroxide scavenger such as copper increases the air oxidation.⁶ Duke⁷ recommends that a lead reductor be placed between the storage container and the buret to reduce any ferric ion that has formed in the titrant.

EXPERIMENTAL

Reagents

Standard Dichromate Solution, 0.1N.

All other reagents were analytical-reagent grade.

Procedure

Titrate the ferrous solutions with the standard dichromate solution to a potentiometric end point.

RESULTS AND DISCUSSION

Several exploratory tests with reagents added to ferrous sulfate in dilute H_2SO_4 gave negative results. These tests include the addition of 0.5N ferric ammonium sulfate, the addition of the peroxide scavenger molybdenum as 0.25% ammonium molybdate, and the addition of cobalt or nickel sulfates in 0.1M concentration. Protection of the solution from light had no effect on the decay rate.

More promising was the addition of sulfamic acid. The stability of partially filled containers at 26° to 28°C under laboratory conditions of continual use is approximately double that of the ferrous sulfate in dilute H_2SO_4 . Best results are obtained

when the ferrous sulfate is dissolved in 15% sulfamic acid and filtered. Lower concentrations of sulfamic acid are less effective. The addition of either H_2SO_4 or NH_4OH hinders the effect of the sulfamic acid as does ammonium nitrate. Finally, ferrous ethylenediammonium sulfate plus the sulfamic acid was not as stable as the ferrous sulfate plus sulfamic acid. The data are shown in Table 1.

TABLE 1
INFLUENCE OF SOLUTION COMPOSITION ON THE RATE OF DECAY OF
FERROUS SOLUTIONS AT 27°C

<u>Solution Composition</u>	<u>Decay Rate, %/hr.</u>	<u>Time Tested, hr.</u>
0.1N FeSO_4 ,	0.011	123
0.7N H_2SO_4	0.010	480
0.1N FeSO_4 ,	(no stabilization, precipitation of double salts)	
0.7N H_2SO_4 , and		
0.1M cobalt and nickel sulfates		
0.1N FeSO_4 ,	0.009	96
0.7N H_2SO_4 , and 0.25% ammonium molybdate		
0.1N FeSO_4 ,	0.004	141
15% sulfamic acid	0.005	260
	<u>0.007</u>	240
Average	0.005	
0.1N FeSO_4 ,	0.009	94
0.7N H_2SO_4 , and 15% sulfamic acid		
0.1N FeSO_4 ,	0.006	66
7% sulfamic acid		
0.1N FeSO_4 ,	0.009	92
7% sulfamic acid, and 1.0% ammonium nitrate		
0.1N FeSO_4 ,	0.010	45
15% sulfamic acid, and 5% ammonium hydroxide		
0.1N $\text{FeC}_2\text{H}_4(\text{NH}_3)_2(\text{SO}_4)_2$,	0.007	171
15% sulfamic acid		

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A BRIEF STUDY ON THE DETERMINATION OF FREE ACIDITY IN CERIC AMMONIUM NITRATE SOLUTIONS

A. W. Wenzel and C. E. Pietri

Existing methods for determining free acid in plutonium(IV) solutions include the iodate precipitation¹ and the citrate complexing methods.² In these methods, the free acid is titrated with standard base after the hydrolyzable plutonium ion is either removed as the insoluble iodate or complexed with citrate. At the Los Alamos Scientific Laboratory (LASL), acceptable results have been obtained by the iodate procedure but values high by 6 to 9% have occurred when complexation was used.³

When ceric ammonium sulfate solutions were used at LASL to simulate plutonium(IV) nitrate solutions, high results were obtained by both methods: +3% and +7% for the iodate and citrate method, respectively. In the present study, these two methods were applied to a ceric ammonium nitrate solution to evaluate the usefulness of this material to serve as a simulated plutonium(IV) solution for the determination of free acidity.

EXPERIMENTAL

Reagents and Apparatus

Potassium Iodate Solution, 0.3M, adjusted to pH 4.3 with dilute HNO_3 .

Sodium Citrate Solution, 10%, adjusted to pH 8.3 with dilute HNO_3 .

Sodium Hydroxide Solution, 0.3M, standardized against National Bureau of Standards SRM No. 185d potassium acid phthalate.

Ceric Ammonium Nitrate Solution, 25 mg./ml., 2.42N in free HNO_3 . This solution also contained a trace of ^{239}Pu so that it had to be analyzed in a glove box.

pH Meter, with glass and saturated calomel reference electrodes.

Microburet, 5-ml. capacity with 0.02-ml. graduations.

Procedures (for plutonium)

Iodate Precipitation. To 50 ml. of the iodate solution in a 100-ml. beaker, add with stirring an aliquot of the sample solution containing 50 mg. or less of plutonium. After a few minutes, filter the mixture through Whatman No. 42 paper, collecting the filtrate in a 250-ml. beaker. Wash the precipitate and paper with two 25-ml. portions of the iodate solution, combining the washes with the

filtrate. Titrate the stirred solution with the standard base and determine the end point graphically. Determine a blank by titrating 100 ml. of the iodate solution in the identical manner.

Complexation with Citrate. Place 30 ml. of the citrate solution in a 100-ml. beaker and measure the pH of the stirred solution. Add an aliquot of the sample solution containing 25 mg. or less of plutonium. Immediately titrate the solution with standard base until the pH reaches the original value.

RESULTS AND DISCUSSION

Replicate aliquots of the ceric ammonium nitrate solution were analyzed by the identical methods described for plutonium. The data, shown in Table 1, indicate that the "iodate" values are about 5.4% low whereas the "citrate" values are 2.5% high on the basis of the prepared value. These errors differ from those obtained by LASL on ceric ammonium sulfate solutions. At least part of the difference may be due to the different anion in the simulated solutions.

TABLE 1

DETERMINATION OF FREE ACID IN CERIC AMMONIUM NITRATE SOLUTIONS

Sample No.	Free Acid, N	
	Iodate Method	Citrate Method
1	2.30	2.48
	2.27	2.49
2	2.29	2.47
	2.29	2.49
	2.28	
3	2.30	2.48
	2.30	2.44
4	2.33	2.52
	2.29	2.52
5	N.A.	2.45
	N.A.	2.47
Average	2.29	2.48

N.A. = No analysis

Additional aliquots of the solution were analyzed by the citrate procedure except that varying time periods were used between the complexation and the titration, Table 2. No specific time was given in the original report.² It can be seen that with increasing waiting times the free acidity apparently decreases.

TABLE 2

THE EFFECT OF DELAY PRIOR TO TITRATION ON THE DETERMINATION
OF FREE ACID IN CERIC AMMONIUM NITRATE SOLUTION BY THE
CITRATE METHOD

Delay, hr.:	Free Acid, N							
	0	0.25	0.50	1	2	3	4	5
Sample No.								
1	2.44 2.48 2.52	2.42	2.39 2.39	2.28	2.27			
2	2.47 2.49			2.36 2.33				
3	2.52 2.52				2.26 2.28	2.22 2.24 2.23 2.22	2.21 2.22 2.20	2.18 2.19 2.17
4	2.45 2.47			2.32 2.31				
Average	2.49	2.42	2.39	2.32	2.27	2.23	2.21	2.18

During the waiting periods, it was noticed that the solution color changed from yellow to colorless with most of the change occurring within the first hour. It is not known whether or not this color change indicates more complete complexation, or reduction of the cerium(IV) to cerium(III) by reaction with citrate. At any rate, the waiting period directly affects the results obtained by this method. With a 15-min. waiting period, the results were identical to the prepared value. However, any intended use of such an arbitrary procedure should be studied further.

ACKNOWLEDGMENT

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AN EVALUATION OF THE DIRECT FUSION. LEACH-PLUS-FUSION.
AND LEACH-FUSION METHODS FOR THE DISSOLUTION OF
PLUTONIUM DIOXIDE-URANIUM DIOXIDE

A. W. Wenzel and C. E. Pietri

Two common methods used for the dissolution of plutonium materials at the New Brunswick Laboratory (NBL) are nitric-hydrofluoric acid digestion¹ and sodium bisulfate fusion^{1,2}. Samples known to be difficultly soluble by the acid dissolution treatment are usually dissolved by direct fusion. Plutonium dioxide-uranium dioxide is often easily dissolved by the mixed acid treatment, however, a small residue occasionally remains undissolved after a reasonable period. Previous work² has indicated that this small residue may contain a significant amount of plutonium. Therefore, when an undissolved residue is apparent, the analyst must either repeat the dissolution with a new sample and an alternate method (direct fusion) or, as is often the case, treat the residue

When it is not practical to repeat the dissolution, one technique that can be used is to filter the residue, fuse it with bisulfate, and combine both fractions (leach-plus-fusion technique). Another approach is to transfer both the solution and residue to a platinum dish, evaporate to dryness, and fuse the entire sample with bisulfate (leach-fusion-technique).

In this study, the results obtained with the leach-plus-fusion, leach-fusion, and direct fusion techniques are compared and some relative merits of the techniques are noted.

Reagents and Apparatus

Platinum Crucibles and Dishes, with covers.

Filter Paper, Whatman No. 40, 5.5 cm diam, or equivalent

Filtering Apparatus, Buchner funnel, 5.6 cm. diam., with 250-ml. filtering flask.

Other reagents and chemicals have been previously described.²

Procedure

Direct Fusion. This procedure has been described in detail elsewhere.^{1,2}

Leach-Plus-Fusion. Digest samples in 8N HNO₃-0.1N HF solution as described previously¹ for up to 48 hr. Filter any residue by suction and wash three times thoroughly with 8N HNO₃. Transfer the filtrate to a 200-ml Teflon beaker and evaporate to less than 10 ml. Transfer the filter paper to a 25-ml. platinum

crucible, dry under heat lamps, carefully char the paper at about 300°C in a furnace using standard techniques, and ignite at 800° to 900°C to remove carbon. Add about 5 g. of NaHSO₄ to the cool crucible and fuse. Dissolve the melt in 100 ml. of 4N HNO₃, combine with the evaporated filtrate, and dilute to 200 ml. with 12N HNO₃.

Leach-Fusion. Digest the sample in the HNO₃-HF solution as above. Transfer the solution and residue to a 75-ml. platinum dish, evaporate to dryness, fuse with up to 20 g. of NaHSO₄ in a furnace, and dissolve the cooled melt as above.

RESULTS

The data shown in Table 1 indicate that all three techniques give the same assay values. The leach-plus-fusion technique requires a time-consuming filtration, an evaporation to reduce the volume of the collected filtrate, and a fusion of the residue. The leach-fusion technique is simpler since it requires only a transfer from beaker to dish with an evaporation to dryness followed by the fusion.

TABLE 1

COMPARISON OF FUSION, LEACH-PLUS-FUSION, AND LEACH-FUSION METHODS FOR THE DISSOLUTION OF PuO₂-UO₂ SAMPLES

Method	Plutonium Found, %			
	Sample			
	A	B	C	D
Leach-plus-fusion	17.73	11.79	17.75	11.83
	17.74	11.79	17.76	11.83
Leach-fusion	17.74	11.79	17.76	11.82
	17.73	11.80	17.74	11.83
Direct fusion	17.74	11.78	17.76	11.82
	17.74	11.79	17.75	11.83

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THE EFFECT OF HUMIDITY ON LOW-FIRED PLUTONIUM OXIDE SAMPLES

A. W. Wenzel, H. N. Simmons, J. L. Duke, and C. E. Pietri

When calcined at temperatures below 700°C, plutonium dioxide is generally hygroscopic and absorbs water rapidly under ordinary laboratory conditions of 30 to 60% relative humidity (R.H.).¹ Because of this characteristic, the determination of the plutonium content of such material can give erroneous results if the material is not maintained in a sufficiently dry atmosphere until subsamples are weighed. In this report, some quantitative observations on the analysis of certain low-fired inventory samples are described.

EXPERIMENTAL

Apparatus

Dry Box A standard New Brunswick Laboratory (NBL)-type closed glove box was set up as a dry box by loading it with several trays containing a total of 1.5 kg. of magnesium perchlorate and using a small fan to circulate the air. Dew points as low as -78°C were obtained as measured with a Lectrodryer apparatus (McGraw-Edison Co.) Because of the possible hazard of handling magnesium perchlorate in glove boxes and the difficulty of disposing of this material, Linde Molecular Sieve 4A (1/8" pellets) will be used as a desiccant in future operations.

PuO₂ Samples

Set No. 1 Duplicate samples of this material, reported to be low-fired oxide by the shipper, were packaged in 1 in. O.D. by 2 in. tall glass bottles closed with a rigid plastic screw cap and "polyseal" liners. The caps were not taped in place. The bottles were contained inside of a sealed vinyl bag. This bag was further wrapped in "air-bubble" plastic and sealed in a metal can 4 in. O.D. and 6 in. tall. All seals appeared to be intact when the samples were received.

Set No. 2 Duplicate samples of low-fired oxide were packaged in glass bottles with "snap-on" plastic caps which were not taped in place. The bottles were double-bagged in vinyl bags.

Sets No. 3 and No. 4. Two individual samples were packaged in a manner similar to Set No. 1 but without the "air-bubble" material.

Procedure

After the subsampling and other indicated operations carried out in the dry box, analyze the materials by the NBL method ^{2,3}

RESULTS AND DISCUSSION

Set No. 1. When the sealed can was opened in the dry box with $< 1\%$ R.H., the R.H. in the dry box rose to 2 to 3% indicating the presence of moisture in the can. When the R.H. decreased again to $< 1\%$, the plastic bags were opened with no increase in R.H. occurring after this step. Subsamples of one sample were then taken and the initial weights recorded. The weights of these subsamples exposed to the air in the dry box were then noted every 15 min. for the first hour and then periodically for the next 23 hr. The sample bottle was placed in a desiccator containing magnesium perchlorate immediately after taking the subsamples. At the end of the weighing test period, the subsamples were removed from the dry box and analyzed.

The weighing tests showed a slow increase in weight with time, amounting to about 0.1% after 1 hr. and 0.4% after 24 hr. No increase in weight was observed after 24 hr.

The second sample was subsampled in the laboratory under conditions of about 50% R.H. In this case, a rapid increase in weight of 0.3% occurred in 1 hr., and then no further increase was observed.

A final test was carried out by subsampling under the same dry box conditions and igniting the equilibrated subsamples. The ignition was carried out starting with a cold furnace, bringing the temperature to 950°C for 2 hr., removing the samples, cooling in a desiccator containing magnesium perchlorate, and reweighing. The heating and cooling was repeated until a constant weight was achieved, generally only two ignitions being required. The material was then analyzed. This ignited material was stable on weighing, with less than $\pm 0.03\%$ weight change occurring in 1 hr.

The analytical data are shown in Table 1. The shipper reported that his value for the plutonium was higher than the "as is" results by about 1%. This difference may indicate some moisture absorption by the samples before being opened at NBL. The analytical data in Table 1 reflect quite accurately the sample weight changes after equilibration.

Set No. 2. The first subsample in this set, weighed and left in the dry box, lost weight at the rate of about 0.003%/min. until an equilibrium change of about -0.15% was obtained. The second subsample exposed to 50% R.H. gained weight at a rate of about 0.03%/min. until an equilibrium change of +0.16% was obtained. The analytical data are shown in Table 2. The difference in the "as received" assays probably reflect a rapid pick-up of moisture by the second sample upon opening the package in the 50% R.H.

Set No. 3. This sample was opened and weighed in the dry box. The weight was stable for 24 hr. after opening. The identical sample exposed to 50% R.H. gained a maximum of only 0.07% in weight. The assays are shown in Table 3.

TABLE 1
EFFECT OF HUMIDITY ON PuO₂ SAMPLES (SET NO. 1)

Pu, %	
Based on "As Received" Weight	Based on Final (Equilibrium) Weight
< 1% R.H.	
85.82	85.48
85.82	85.49
85.91	85.54
<u>85.86</u>	<u>85.52</u>
Avg. 85.85	85.50
~ 50% R.H.	
85.73	85.45
85.70	85.42
<u>85.71</u>	<u>85.43</u>
Avg. 85.71	85.43
After Ignition ~ 50% R.H.	
87.56	87.56
87.47	87.46
<u>87.49</u>	<u>87.49</u>
Avg. 87.50	87.51

TABLE 2
EFFECT OF HUMIDITY ON PuO₂ SAMPLES (SET NO. 2)

Pu, %	
Based on "As Received" Weight	Based on Final (Equilibrium) Weight
< 1% R.H.: Sample No. 1	
85.39	85.54
85.33	85.44
<u>85.30</u>	<u>85.43</u>
Avg. 85.34	85.47
~ 50% R.H.: Sample No. 2	
85.44	85.22
85.22	85.06
85.21	85.06
<u>85.18</u>	<u>85.04</u>
Avg. 85.26	85.10

TABLE 3
EFFECT OF HUMIDITY ON PuO₂ SAMPLES (SET NO. 3)

Pu, %	
<u>(< 1% R.H.)</u>	<u>(~ 50% R.H.)</u>
87.30	87.23
<u>87.34</u>	<u>87.28</u>
Avg. 87.32	87.26

Set No. 4. This material, opened and weighed in the dry box, was stable with time. The analysis gave a value of 87.41% plutonium. Surprisingly, the shipper reported that this material had been handled in a 10 to 20% R.H. without much regard for the humidity.

The results obtained with these four materials are difficult to interpret and are given chiefly to show the erratic behavior of low-fired plutonium oxide received for analysis. The results point out the need for controlled conditions of relative humidity in the packaging, storage, and shipment of this type of sample. Moreover, there appears to be a great need for low-fired plutonium oxide standards to accompany samples through all phases of operations and final analysis. A multilaboratory evaluation program involving the use of such standards under controlled conditions would hopefully help to solve these problems.

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PACKAGING PLUTONIUM METAL, ALLOY, AND OXIDE ANALYTICAL SAMPLES FOR OFFSITE SHIPMENT

A. W. Wenzel, H. N. Simmons, and C. E. Pietri

Continuing the study¹ of the various factors that affect the analytical results obtained by the New Brunswick Laboratory (NBL), the present report summarizes a study of two types of sample containers used to ship plutonium samples from various sites to NBL for analysis.

Plutonium metal and certain alloys oxidize in the presence of moist air. Plutonium oxide may absorb moisture. Low-fired material is very hygroscopic.² If a sample oxidizes or absorbs moisture on shipment and storage before analysis, obviously it is no longer a representative sample. A highly precise and accurate analysis of such a sample as carried out by NBL not only is a waste of time and money, but also gives an erroneous inventory of the bulk material.

In a study sponsored by the Division of Nuclear Materials Safeguards, samples of plutonium-aluminum (1.5%) alloy and plutonium oxide were packaged in two types of containers at the plant site and were shipped to NBL for plutonium assay.

EXPERIMENTAL

Procedure

Four samples of a Pu-Al alloy and four of a PuO₂ material were prepared and shipped to NBL from a commercial manufacturing site. Two alloy and two oxide samples were packaged in plastic vials with snap-on caps; the other two samples of each material were contained in sealed glass tubes (ampoules) under nitrogen. Although it was not known when these materials were packaged, the samples were in transit 7 days. Within 6 hr. of receipt, one vial and one ampoule of each material were opened, and three portions for analysis were removed from each container. The remaining unopened samples were stored for 38 days under normal glove-box conditions (22° to 25°C, 40 to 60% relative humidity), then the materials were analyzed as before.

The analytical portions were dissolved by standard methods³ and the plutonium was determined by the NBL constant-current potentiometric method⁴ after ion-exchange separation of the impurities.⁵ Observations on the condition of the material on receipt and after storage were also noted.

RESULTS AND DISCUSSION

The data obtained on these four samples are shown in Table 1. The Pu-Al alloy in plastic vials was extensively oxidized on receipt and it appeared to continue to oxidize during the storage period. The initial assay was low by nearly 1.5% from the expected value of 98.5%. After the storage period, the plutonium assay was low by about 2.5%. The alloy in sealed tubes under dry nitrogen appeared to be only slightly oxidized on receipt and the assay values were very near the value expected. After storage a slight increase in oxidation was apparent and the assay was about 0.3% low.

The PuO₂ in the vials or sealed glass tubes showed no visible change. The original plutonium content of this material was not known. The oxide in the plastic vials assayed 0.5% lower than that in the sealed tubes on receipt. After the storage period, the material in both types of containers showed an insignificant change of $\pm 0.1\%$ plutonium from the previous values. If the weight change of the oxide in the plastic vials was actually due to absorption of moisture, the change occurred before receipt of the samples. However, the higher value of the oxide in sealed tubes could have been caused by loss of moisture on sealing the tubes. This test should be repeated with low-fired and dry oxide of known assay.

TABLE 1

ASSAY VALUES OF PLUTONIUM-ALUMINUM ALLOY AND PLUTONIUM OXIDE
PACKAGED IN PLASTIC VIALS AND SEALED GLASS TUBES

	<u>Container</u>	Elapsed Time Before Analysis,	<u>Pu, %^a</u>	<u>Appearance of Sample</u>
		<u>Days</u>		
Pu-Al	Plastic vial	7	97.07	Badly corroded
		45	95.76	Very badly corroded
	Sealed glass tube	7	98.32	Very slightly corroded
		45	98.00	Slightly corroded
PuO ₂	Plastic vial	7	84.98	No unusual appearance
		45	85.07	" " "
	Sealed glass tube	7	85.48	" " "
		45	85.38	" " "

a. Average of 3 determinations.

The plutonium alloy results clearly indicate that shipment of this type of material must be made in sealed glass tubes to obtain representative analytical data. This precaution was observed by Los Alamos Scientific Laboratory in their preparation and packaging of plutonium metal distributed by the National Bureau of Standards as a reference material. This plutonium metal was sealed in

ampoules purged with dry inert gas and partially evacuated before being sealed. The assay values have not changed for several years.

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A MODIFIED AMPEROMETRIC METHOD OF DETERMINING PLUTONIUM

C. E. Hedrick, C. E. Pietri, A. W. Wenzel, and M. W. Lerner

Existing procedures for the determination of plutonium include those in which the plutonium is oxidized to plutonium(VI) by perchloric acid,¹ persulfate,² or silver(II)³ followed by titration with ferrous ion. Although iron and uranium do not interfere with these procedures, other serious interferences remain: manganese, cerium, chromium, and vanadium. This general method would be much more valuable if these interferences could be eliminated.

In the present work it was found that the interference of manganese, cerium, and chromium can be eliminated by selective reduction with arsenic(III) in the presence of a catalytic quantity of osmium tetroxide before the titration of the plutonium(VI) is carried out. The plutonium(VI) is not reduced to any measurable extent by the arsenic(III) within the 5-min. reaction period. Vanadium, however, is not reduced quantitatively under these conditions. On the other hand, the final interference of vanadium is quantitative and a correction for its presence can be made.

Another improvement consists of the use of a dilution and reaction medium of 1N sulfuric acid, 0.5N nitric acid, and 0.35% ammonium molybdate. When this diluent is used, the nitric acid slows up the reaction between silver(II) and diluting solvent and assists in dissolving any silver oxide sediment, the sulfuric acid complexes plutonium(IV) and speeds up the reaction between iron(II) and plutonium(VI), and the molybdenum makes possible the determination of a reliable blank in the absence of plutonium. Without molybdenum present, a brown color forms in the blank reagent mixture and high reducing values are obtained. The mechanism of the reaction involving molybdenum is not known at present.

The excess arsenic(III) is removed by visual titration with permanganate which also oxidizes any vanadium(IV) back to vanadium(V). Excess permanganate is reduced by oxalic acid. The solution is titrated amperometrically with iron(II) to a slight excess which is back titrated with dichromate.⁴

In the analyses of plutonium samples to which are added up to 5000 ppm. iron, 3000 ppm. chromium, 1000 ppm. manganese and cerium, and 20% uranium, the precision and accuracy appear to be about 0.05% when the results are compared to the reliable but slower NBL ion exchange-bipotentiometric titration method.⁵ A more detailed report of this work has been published in *Analytical Chemistry*, 44, 377 (1972).

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DETERMINATION OF URANIUM IN NATURAL WATERS BY ELECTRICAL- DETECTION SPARK-SOURCE MASS SPECTROMETRY

E. L. Callis

Numerous methods exist for the determination of uranium in natural waters. These include neutron activation,¹ isotope-dilution mass spectrometry,² fluorometry,³ and polarography.⁴ With the exception of neutron activation, these methods require rather extensive chemical separations and preconcentrations. At the New Brunswick Laboratory (NBL), a spark-source mass-spectrometric method, which in most cases requires no separations or preconcentrations, has been developed. If a separation is necessary, a relatively simple ammonium hydroxide precipitation with iron carrier is used. The separation technique is required with samples having a uranium content below 1 $\mu\text{g./l.}$ or having a high concentration of dissolved solids as is found in seawater.

The method consists of incorporating the impurities obtained by evaporation into a bismuth oxide matrix. This mixture is then combined with graphite and pressed into electrodes. The electrodes are sparked and the $^{238}\text{U}/^{209}\text{Bi}$ ratio measured with a dual collection system. By comparison with a standard containing a known amount of uranium, the uranium content of the sample can be determined.

EXPERIMENTAL

HNO_3 , distilled.

Bismuth Nitrate Solution, prepared by dissolving 3 g. of high-purity bismuth metal in HNO_3 and diluting the solution to 100 ml.

Ammonium Hydroxide, prepared from tank ammonia.

Iron Carrier Solution, 10 mg./ml., prepared by dissolving pure iron wire in HNO_3 .

Uranium Solution, 5 $\mu\text{g./ml.}$, prepared by dissolving uranium metal in HNO_3 and diluting to an appropriate volume.

Spark-Source Mass Spectrometer. The instrument is an Associated Electrical Industries Ltd. (AEI) Model MS-7 modified for electrical detection by the manufacturer. This instrument has been further modified by the author to allow the simultaneous collection of the ^{209}Bi ion beam and one of the uranium isotopes from ^{234}U to ^{238}U . This modification was made because the normal method of collecting a portion of the total ion beam as a reference signal before mass separation did not yield the desired precision, particularly with graphite electrodes.

Procedure

Electrode Preparation with Fresh Water Samples Pipet a 20-ml volume of sample and 5 ml of the bismuth solution into a 30-ml Vycor crucible and add a few drops of HNO_3 to prevent the bismuth from hydrolyzing. Evaporate the solution to dryness on a hot plate and ignite at 450°C for 10 min in a muffle furnace to convert the bismuth nitrate to oxide. Transfer the oxide to a small plastic mixing vial, and add 1 to 2 volumes of -325 mesh graphite powder and a plastic mixing ball. Mix in a Wig-L-Bug for 1 min. Press the mixture into electrodes with an AEI sample molding die.

Prepare electrodes for the standards similarly by adding a known amount, 10 to 25 μg , of uranium to 20 ml of distilled water and proceeding as above.

Electrode Preparation with Samples Requiring Separation To a 20-ml sample in a 50-ml beaker, add a few drops of HNO_3 and a few drops of iron carrier solution. Boil to destroy carbonate, then add NH_4OH to the hot solution until the solution is alkaline. Filter the precipitate through Whatman No. 41 paper, discarding the filtrate. Dissolve the precipitate off the paper with 2 to 3 ml of warm 1:1 HNO_3 , collecting the solution in a 30-ml Vycor crucible. Proceed as with fresh water samples.

Measurement of U/Bi Ratio Integrate the signal from the bismuth on the plate collector to a given charge. Simultaneously, measure with a digital voltmeter the output of the multiplier signal integrated by the Amplifier and Scan Control Unit (ASCU) of the electrical detection system.

Calibration of System Measure the U/Bi ratio of a standard electrode having a known U/Bi ratio. Measure the ratio at the beginning and end of a series of sample runs since the ratio is a function of the multiplier gain and the monitor-integrator trip-point, both of which are subject to drift.

RESULTS AND DISCUSSION

In the modified instrumental system the ^{209}Bi beam is collected on the plate collector because it is very large as compared to the uranium peaks. This signal is amplified and integrated by the original MS-7 monitor-integrator amplifier. The uranium beam of interest is collected on an electron multiplier, the signal from which is amplified and integrated by the ASCU.

In practice only the ^{238}U peak is measured since in normal uranium the ^{235}U peak is less than one hundredth of the total uranium. The sample can be checked for a high ^{235}U content at the beginning of an analysis when the uranium region of the spectrum is displayed on the oscilloscope for alignment of the beams onto the slits. If the ^{235}U enrichment is high, the ^{235}U beam can be measured by adjusting the accelerating voltage to bring the ^{235}U beam onto the multiplier slit.

In Table 1 are given some typical results with the proposed method and the comparative data obtained fluorometrically on actual ground water samples.

TABLE 1
COMPARISON OF RESULTS OBTAINED BY PROPOSED METHOD
AND BY FLUOROMETRY

Sample No.	Uranium, g./l.	
	Proposed Method	Fluorometry
1	0.00175	0.0018
2	0.00109	0.0012
3	0.00056	0.00059
4	0.00324	0.00324
5	0.000067	0.00007
6	0.000019	0.00002

At the present time, the chief factor that limits the precision of the proposed method is the reproducibility with which the electrodes can be positioned between runs. The precision within a run is 2 to 3%, and between runs is 4 to 5%. A telescope alignment device is presently being fabricated to minimize this source of error.

A relatively large blank corresponding to 0.05 μg . of uranium presently limits the minimum amount that can be determined reliably to about 0.02 μg . However, the instrument is capable of detecting a signal from 10 to 100 times smaller than the signal corresponding to 0.02 μg . The blank, therefore, is the limiting factor in the smallest amount of uranium that can be determined.

An advantage of the proposed method is that the entire mass range can be scanned for less precise (± 30 to $\pm 40\%$) determinations of other elements in the sample. A complete scan takes about 15 min.

For the uranium determination only, from 8 to 10 samples can be analyzed in a day if no separations are required. If separations are required, from 5 to 6 samples can be analyzed daily.

ACKNOWLEDGMENT

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EXTENSION OF THE REFRACTORY CARRIER-LAYER METHOD TO THE DETERMINATION OF OTHER ELEMENTS IN URANIUM

H. G. Yuster

In a previous report,¹ the determination of the refractories titanium, niobium, and zirconium in U_3O_8 by the use of a silver chloride-uranium tetrafluoride carrier-layer technique was described. This same technique has now been extended to the determination of iron, nickel, manganese, copper, and aluminum.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus are identical to those given in reference (1) with the following additions:

Cobalt Oxide, reagent-grade.

U_3O_8 , ultra-pure, prepared by Union Carbide Corporation, Y-12 Site.

Ethyl Alcohol, reagent-grade.

Procedure

Preparation of Internal Standard. Weigh 5.0 g. of silver chloride and 25.0 mg. of cobalt oxide into an 8-cm. agate mortar. Add sufficient alcohol to form a loose paste and mix, but do not grind, with the pestle. Continue mixing gently until the alcohol is nearly evaporated and allow to air dry. Scrape the mortar down with an index card, and repeat the alcohol addition, mixing, and scraping down three more times.

Prepare the standards, the carrier-layer mixes, and the electrode charges, and use the exposure conditions as described in reference (1). Use both plates in the plate holder to obtain the entire range of wavelengths from 2900 to 3550 $\text{\AA}$ in the second order.

Calculations. Use the internal standard cobalt line at 2521.36 $\text{\AA}$ for the log I ratios of iron and manganese on the first plate; the cobalt line at 3044.00 $\text{\AA}$ for the nickel, aluminum, and copper on the second plate.

RESULTS AND DISCUSSION

The wavelengths used and the estimated limits of sensitivity together with the range of the standards are given in Table 1.

TABLE 1

WAVELENGTH, SENSITIVITY, AND RANGE OF STANDARDS

Element	Wavelength, Å	Limit of Sensitivity, ppm	Range of Standards, ppm.
Co	2521.36	--	internal standard
Fe	2599 40	2	2-200
Mn	2794 82	0 5	0.2-20
Co	3044 00	--	internal standard
Ni	3002 49	2	2-200
Al	3082.16	2	2-200
Cu	3247 54	0 2	0.2-20

Ten samples of uranium metal were converted to U_3O_8 and analyzed by both the proposed procedure and by the routine New Brunswick Laboratory (NBL) gallium oxide carrier-distillation procedure, Table 2. Examination of the data shows good agreement for all five elements. In most cases the differences are within the usual spectrochemical precision.

TABLE 2

COMPARISON OF GALLIUM OXIDE CARRIER (GA) AND PROPOSED CARRIER-LAYER (CL) RESULTS

Sample	Fe		Ni		Mn		Cu		Al	
	GA,	CL	GA,	CL	GA,	CL	GA,	CL	GA,	CL
1	130,	150	50,	45	13,	10	12,	8	16,	29
2	115,	110	38,	32	12,	14	7,	5	11,	10
3	3000,	>200	110,	100	50,	40 ^a	20,	25	60,	58
4	165,	175	38,	32	10,	11	22,	25	10,	11
5	150,	130	50,	44	12,	10	10,	7	18,	17
6	140,	125	26,	50	12,	8	15,	13	20,	22
7	120,	130	48,	44	12,	9	11,	8	20,	25
8	130,	135	50,	40	10,	6	18,	13	22,	25
9	600,	>200	75,	80	23,	21	17,	14	290,	230 ^a
10	145,	140	60,	56	12,	11	20,	19	24,	27

a extrapolated value

The advantages of the proposed procedure over the gallium oxide procedure are: (1) it is possible to determine the given elements plus the refractories titanium, niobium, and zirconium on the same spectral plates (2) an improved sensitivity for aluminum, iron, nickel, and manganese is obtained One dis-

advantage of the procedure is an increase in background and the presence of uranium lines. The latter effect is minimized with the use of second order exposures and a narrow slit which in most cases pulls the interfering lines apart. However, the uranium line at 2835.63 Å does interfere with the chromium line to make this determination difficult. The chromium line at 4254.35 Å could be used without interference but it requires exposure at another wavelength range. It is hoped that additional work can be carried out to evaluate the method for other uranium materials such as the tetrafluoride and the nitrate.

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THE SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN ALUMINUM-URANIUM ALLOYS

H. G. Yuster and R. L. Graff

The application of the carrier-distillation technique to the determination of impurities in uranium-aluminum alloys is generally unsatisfactory. The conversion to the mixed oxides necessitates a lengthy dissolution step. In addition, comparable standards should be used in the measurements and such standards are not available. If reliance is placed upon U_3O_8 standards, the aluminum matrix effect gives poor accuracy. Even if the oxides are diluted 1:100 with pure uranium, the aluminum matrix effect is still appreciable.

Because of these factors, a procedure was developed that involves the use of a gallium fluoride-graphite buffer and a complete burn of the sample. With this procedure, no conversion of the sample is needed and National Bureau of Standards (NBS) analyzed aluminum alloys are used as standards. The procedure has been applied to actual alloy samples which were also analyzed by atomic absorption spectrophotometry.

EXPERIMENTAL

Reagents and Apparatus

Gallium Fluoride, prepared by reaction of 99.9999% gallium metal (Alusuisse Metals, Inc.) with HF purified by distillation from platinum.

Graphite, National Carbon SP-2 powder.

Standards, NBS No. 85a, 85c, and 87.

Mixing Vials, polystyrene, 1/2 in. O.D. x 1 in. long, and 3/8 in. plexiglass ball, Spex Industries.

Spectrograph, Jarrell-Ash 3.4 Ebert, 15,000 lines/in. grating, 2.5 Å/min. dispersion, set for 2900-3550 Å in second order; Jaco Varisource.

Densitometer, Jarrell-Ash microphotometer.

Calculating Board, Applied Research Laboratories.

Procedure

Preparation Buffer Mixture Weigh 250 mg. of gallium fluoride and 250 mg. of graphite into the mixing vial and shake in a Wig-L-Bug for 2 min.

Preparation of Standards and Samples. Hold a turning of each standard in a locking forceps and obtain filings with a new flat fine file that has been degreased with carbon tetrachloride and then brushed well to remove iron particles. Obtain filings of samples, generally in the form of sheets, in a similar manner.

Electrode Loading. Weigh 4.0 mg. of buffer mixture into the electrode cup and place 1.0 mg. of sample or standard filings on top of the buffer. Carefully mix filings and buffer with a small spatula.

Exposure Conditions

Electrodes : upper, ASTM C-1
lower, UCC U7-1991

Excitation : 14 A. (shorted), 220 VDC

Electrode Gap: 4 mm.

Slit : 25 μ wide, 9.1 mm. high

Sector : 7 steps rotating

Step Ratio : $I_0/I = 2$

Plate : 4 x 10 in. Eastman Kodak
Spectrum Analysis No. 1

Processing : D-19, 3 min.
short stop, 30 sec.
Kodak Rapid Fixer, 2 min.
wash, 2 min.

Determination of Concentrations. Table 1 lists the wavelengths used, the concentration range of the elements in the standards, and the method of determining the concentration for each element. Aluminum was used as an internal standard for two elements; it was not suitable for the other elements. In the "direct" method given in Table 1, the log of the relative intensity of the element was used in the calibration curve and in the calculations of concentrations in the sample. In the "visual" method, simple visual comparisons with one standard only was used. (The concentrations of these elements in the other two standards are too high to be measured.)

RESULTS AND DISCUSSION

Two buffers initially used were graphite and a lithium fluoride-graphite mixture. It was found that these buffers fail to give complete burns of samples and standards. The gallium fluoride-graphite mixture gives a satisfactory burn with a minimum of background.

TABLE 1
WAVELENGTH, RANGE OF STANDARDS, AND ANALYTICAL METHOD

Element	Wavelength, Å	Concentration Range of Standards. %	Analytical Method
Cr	4289.72	0.03 - 0.17	direct
Cu	3273.96	0.30 - 7.92	visual
Fe	2599.40	0.21 - 0.46	direct
Mg	2852.13	0.002 - 1.58	visual
Ni	2050.82	0.03 - 0.59	direct
Si	2506.90	0.11 - 6.11	internal standard
Ti	3349.41	0.016 - 0.61	internal standard
Al	2378.41	internal standard	--

Table 2 gives the results obtained by the proposed procedure on four actual production samples along with results obtained by atomic absorption spectrophotometry. The data are in good agreement for all the elements reported except titanium. The discrepancy in the titanium values must still be resolved. No atomic absorption spectroscopic values were obtained for manganese. The emission values given show adequate sensitivity with 1 mg. of sample.

TABLE 2
COMPARISON OF RESULTS OBTAINED BY EMISSION SPECTROGRAPHY (ES)
AND ATOMIC ABSORPTION SPECTROPHOTOMETRY (AA)

Sample	Concentration, % (on sample basis)							
	Cr		Cu		Fe		Mg	
	ES	AA	ES	AA	ES	AA	ES	AA
1	0.02	0.03	0.005	0.004	0.05	0.04	0.001	0.004
2	0.02	0.014	0.1	0.1	0.4	0.4	0.001	0.001
3	0.04	0.03	0.1	0.1	0.4	0.4	0.001	0.001
4	0.01	0.01	0.005	0.006	0.1	0.1	0.001	0.001
	Mn		Ni		Si		Ti	
	ES	AA	ES	AA	ES	AA	ES	AA
1	0.005	--	0.006	0.006	0.07	0.07	0.009	0.10
2	0.04	--	0.01	0.01	0.15	0.12	0.014	0.005
3	0.01	--	0.02	0.02	0.08	0.07	0.012	0.005
4	0.002	--	0.01	0.01	0.08	0.07	0.013	0.008

ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN BORON AND BORON CARBIDE

R. L. Graff and H. G. Yuster

Some uncertainty in the silicon values in boron materials obtained by emission spectrography¹ at the New Brunswick Laboratory (NBL) prompted the study of this determination by atomic absorption spectrophotometry. The procedure developed was straightforward: fusion of the boron or boron carbide in potassium carbonate followed by measurements on the resulting solution. The presence of boric acid in the solutions could be tolerated when certain precautions were taken. Comparative analyses by emission spectrography and the proposed procedure were made on several samples of boron and boron carbide.

EXPERIMENTAL

Reagents and Apparatus

Potassium Carbonate, anhydrous

Standard Silicon Solution, 1 mg./ml., prepared from sodium metasilicate.

Boric Acid, analytical reagent.

Atomic Absorption Spectrophotometer, Perkin-Elmer Model No.403 with silicon hollow cathode lamp (Intensitron No. 303-6063) and nitrous oxide-acetylene burner.

Procedure

Dissolution of Sample. Fuse a 0.3-g. sample with 4 g. of potassium carbonate in a 50-ml. platinum crucible, previously lined with 2 g. of the carbonate, over a blast burner. Dissolve the cooled melt in water, dilute to 100 ml. with water, and store the solution in a polyethylene bottle.

Preparation of Standard Solutions. Dissolve 6.0 g. potassium carbonate and 0.3 g. of boron as boric acid in water, add the appropriate aliquots of the standard silicon solution, and dilute to 100 ml.

Analysis. Obtain the atomic absorption spectrophotometric measurements with the nitrous oxide-acetylene flame following the general procedure given in the Perkin-Elmer manual. Use the 2516 Å silicon line and the 10X absorbance read-out in the 100-average mode. Compare the absorbance of the sample with the standard curve of absorbance vs. concentration prepared from the standards.

RESULTS AND DISCUSSION

In initial runs of boric acid solutions with the instrument in the "100-average" mode which gives an average of 100 individual measurements in 11 sec. it was observed that the absorbance gradually dropped upon continued measurement after 30 to 40 sec. When a standard previously measured was tested again at this time, the absorbance was now lower than that previously found. This phenomenon was traced to incipient clogging of the capillary and atomizer. Sequential aspiration of 1 l HNO_3 for 10 sec., water, and then the standard and sample solutions gave the original absorbances. This clean-out technique is recommended between each boric acid solution aspirated.

Measurements were made of potassium carbonate solutions containing silicon with and without added boric acid. The boric acid had no significant effect on the absorbance. It was also found that the blank silicon values in the standards (and sample) solutions came chiefly from the potassium carbonate. The silicon content of the potassium carbonate is about 35 ppm.

This silicon blank in the potassium carbonate is much lower than that in the various lots of sodium carbonate tested. Two other factors made potassium carbonate a better choice than the sodium salt for the fusion dissolution: (1) the fusion cake dissolved easier; (2) the solution containing potassium does not produce the intense yellow sodium pillar of flame which can be annoying during the measurements.

The results obtained by both the proposed procedure and emission spectrography are shown in Table 1. The agreement between the two techniques can be seen to be only fair with appreciable differences existing for elemental boron samples F4360, F5702, and F5881 and the carbide sample. In regard to the carbide sample, later work on a different problem indicated that this material is segregated; therefore, the difference found here may not be significant. Because of the differences in the results of the elemental samples, additional analyses were made on F5868 and F5881. With both samples, the new value was nearly identical with the previous one: F5868, 2750 ppm.; F5881, 1170 ppm. A further analysis was made of F5881 by dissolving it by an acid treatment¹ prior to the measurement. The result was 1330 ppm.

These data indicate the possibility of some error in the emission spectrographic results for silicon in boron. Additional work is planned to resolve this problem when time permits.

TABLE 1

COMPARATIVE RESULTS FOR SILICON BY ATOMIC ABSORPTION
AND EMISSION SPECTROGRAPHY

<u>Samples</u>	<u>Si, ppm.</u>	
	<u>Atomic Absorption</u>	<u>Emission Spectrography</u>
NBL F-4078	367	250
F-4359	1950	2000
F-4360	1300	1900
F-5702	2430	3200
F-5868	2800	2400
F-5881	1230	600
F-6109	6300	5900
Boron Carbide	6300	4100

REFERENCE

1. Yuster, H. G. and Mullin, H. R., NBL-210 (June 1964), p. 21.

A TENTATIVE GAMMA-RAY SPECTROMETRIC METHOD FOR THE DETERMINATION OF RADIUM-226 IN SOIL SAMPLES

L. C. Nelson, Jr

The most convenient existing method¹ for determining ^{226}Ra involves separation of the isotope by coprecipitation with barium sulfate in the presence of citrate. reprecipitations by pH adjustment with excess acetic acid after dissolution in ethylenediamine-tetraacetic acid (EDTA) and ammonia, and finally by alpha counting the purified barium sulfate. When this method is applied to soil samples. the dissolution of the soil is tedious and time-consuming, and the presence of large concentrations of other elements that precipitate from EDTA solution on adjustment of the pH by excess acetic acid makes this decontamination step unattractive. Accordingly, a direct gamma-ray spectrometric method was sought

It was found that the 186-keV gamma-ray peak from radium is suitable for this measurement. Although more suitable gamma rays can be found in the radium decay series, the choice of the 186-keV. peak was made because it is not affected by any loss of radon during sample preparation. Possible interference from uranium is determined by carrying out a fluorometric uranium analysis. Uranium is generally absent in these samples

EXPERIMENTAL

Apparatus

Vials, glass, machine-made 4-dram capacity

Scintillation Detectors, 3 in. x 3 in. NaI(Tl)-type with a 1-in. diam. by 2-in. deep well

Multichannel Analyzer, 256 channel, hard-wired RCL Model 20623 with a data-summation attachment and typewriter print-out.

Procedure

Dry the soil at 110°C , ignite at 600°C , and grind in a mortar to a uniform fine powder. Place a weighed portion in the glass vials. Accumulate the gamma-ray spectrum for a 1-hr. period and integrate the area under the 186-keV. peak. Calculate the concentration of ^{226}Ra in microcuries per kilogram of original material by means of a calibration factor determined by measuring in an identical manner the activity of a NBS ^{226}Ra standard appropriately diluted with water. Perform the calculation by means of a FOCAL computer program reported elsewhere ²

RESULTS AND DISCUSSION

A NaI gamma-ray spectrum of the ^{226}Ra decay series is shown in Figure 1. It can be seen that the 186-keV. ^{226}Ra peak is sufficiently resolved for measurement.

Self-absorption in the measurements of the soil samples was not considered to be a serious source of error because the soil densities of about 1.2 g./ml. are similar to the aqueous solutions of the standards and do not vary greatly among themselves.

The results obtained with a series of actual soil samples are shown in Table 1. Also shown in Table 1 are the nickel concentrations determined spectrochemically. In the absence of samples with known ^{226}Ra content, the qualitative relation between the ^{226}Ra and the nickel concentrations can be taken as a rough measure of the validity of the ^{226}Ra values on the basis that both the nickel and ^{226}Ra values arise from a common source, that of a uranium-bearing residue.

TABLE 1
RADIUM-226 AND NICKEL CONTENT OF SOIL SAMPLES

Sample Weight, g.	^{226}Ra ,	Ni, ppm.
	$\mu\text{Ci/kg. Sample}$	
19.1357	6.5×10^{-1}	1200
19.2629	1.3×10^0	1700
18.5725	1.6×10^{-1}	650
19.3024	8.3×10^{-2}	90
17.9160	9.4×10^{-2}	110
19.1186	9.3×10^{-2}	120
17.6859	9.2×10^{-2}	30
19.0571	2.9×10^{-2}	30
17.5985	4.2×10^{-2}	35
17.2283	3.5×10^{-2}	50
16.3305	2.8×10^{-2}	40
16.3825	4.4×10^{-2}	30
16.1509	4.9×10^{-2}	40
18.3435	3.9×10^{-2}	50
16.0623	5.6×10^{-2}	35

The method has potential for materially reducing the time required for this type of determination, but further work must be carried out to establish its reliability. Although the reliability of the results may prove to be insufficient for some purposes, it should be adequate for rapid environmental surveys.

REFERENCES

1. Goldin, A. S., Anal. Chem., **33**, 406 (1961).
2. Nelson, L. C., Jr., NBL-262 (January 1972), p. 68.

FIGURE 1. NaI GAMMA-RAY SPECTRA OF ^{226}Ra DECAY SERIES

A FOCAL COMPUTER PROGRAM TO CALCULATE SOIL AND WATER RADIOACTIVITIES

L. C. Nelson, Jr.

Soil and ground water samples from areas where thorium and uranium ores and residues have been stored are periodically analyzed to ensure that contamination of the ground water supply does not occur. The samples are analyzed for total alpha and beta activities and for ^{226}Ra and ^{228}Ra . The calculations of these activities, which are reported in microcuries per kilogram of sample, involve background corrections, factors for efficiency and aliquoting, and, for soil samples, corrections for moisture content. These calculations are tedious and the possibility of errors is high because these corrections and factors are different for each sample and type of analysis. To facilitate the calculations and to reduce the chance for errors, a short computer program was written in the FOCAL language.

EXPERIMENTAL

Computer System. FOCAL is an interactive service program designed to solve numerical problems. FOCAL is available to any Digital Equipment Corporation PDP-8 or PDP-9 series computer or any PDP-15 system. This particular program was written on a PDP-15 system.

Program. A listing of the program is shown in Figure 1. It is written in four sections: one each for the calculations of total alpha and total beta activities, and two for the calculations of the ^{226}Ra and ^{228}Ra activities. The first of the latter two sections calculates the activity of ^{226}Ra as obtained by a barium-carrier separation procedure¹ or of the ^{228}Ra obtained by a lanthanum-carrier and 2-propanol dry extraction method,² as applied to water samples. The second is used for a gamma-spectrometric method for the direct measurement of ^{226}Ra in soil samples. Each section is reentrant in that it will repeat the calculations until all samples are completed, at which time a "Q" (for quit) is typed instead of the sample number to make the program proceed to the next section.

The running program, Figure 2, is written in a tabular format. This format ensures that pertinent factors are not forgotten and allows the sample calculation to be repeated if a typing error is made. The counting constants are requested at the start of each section since they are used in each calculation of the section. In addition, this step makes the program modular, that is, it can be entered at the beginning of each section. Sample numbers, count rates, and other factors are requested under their respective table headings. If a factor is not required for a given set of samples, e.g. wet/dry factor for soil samples, a value of 1 must be typed to obtain correct results. All responses must be terminated by an

```

C FOCALIS V64
01.05 T "ENVIRONMENTAL CONTROL PROS",!!
01.10 A "ALPHA EFF.=",A1,I
01.20 A "ALPHA BKG.=",A3,I
01.30 T "SAMPLE # ALPHA C1. WET/DRY MICROCURIES/Kg",!
01.40 A SN; IF (SN-17)1.5,2.13; A " " "AC," "WD
01.50 SET AC=(AC-A3)/A2
01.60 SET MC=(AC*200)/2.22*1016*WD
01.70 T 2," " "MC,I
01.80 GOTO 1.40
02.10 A "BETA EFF.=",B1,I
02.20 A "BETA BKG.=",B3,I
02.30 T "SAMPLE # BETA C1. WET/DRY MICROCURIES/Kg",!
02.40 A SN; IF (SN-17)2.5,3.37; A " " "BC," "WD
02.50 SET BC=(BC-B3)/B2
02.60 SET MC=(BC*200)/2.22*1016*WD
02.70 T 2," " "MC,I
02.80 GOTO 2.40
03.30 T "SAMPLE # 226 Cf. WET/DRY RECOVERY MICROCURIES/Kg",!
03.40 A SN; IF (SN-17)3.5,4.13; A " " "RC," "WD," "RE
03.50 SET RC=(RC-A3)/A2; SET RC=[RC*WD]/RE
03.60 SET MC=(RC*2/2.22*1016)
03.70 T 2," " "MC,I
03.80 GOTO 3.40
04.10 A "GAMMA CALIBRATION=",CAL," C/MICROCURIE.",I
04.20 A "GAMMA BKG.=",G3,I
04.25 A "COMPTON BASELINE=",BL,I
04.30 T "SAMPLE # GAMMA C1. WET/DRY GMS/VIAL MICROCURIES/Kg",!
04.40 A SN; IF (SN-17)4.5,5.13; A " " "GC," "WD," "
04.50 SET MC=(GC-BL-G3)*WD
04.60 A ,GV; SET MC=[(MC/GV)/CAL]*1000
04.70 T 2," " "MC,I
04.80 GOTO 4.40
05.10 T "END OF JOB.",!!!

```

*

FIGURE 1. PROGRAM LISTING

*JO

ENVIRONMENTAL CONTROL PROG

ALPHA EFF.=:0.408

ALPHA BKG.=:0.6

SAMPLE #	ALPHA CT.	WET/DRY	MICROCURIES/KG
:F6455	:2.5	:1.00	= 0.419537184E-03
:F6456	:2.9	:1.00	= 0.507860801E-03
:F6457	:4.8	:1.00	= 0.927397935E-03
:F6458	:5.4	:1.00	= 0.105938341E-02
:F6459	:0.4	:1.00	= -0.441618088E-04

:Q

BETA EFF.=:0.48

BETA BKG.=:2.2

SAMPLE #	BETA CT.	WET/DRY	MICROCURIES/KG
:F6455	:5.8	:1.00	= 0.675675675E-03
:F6456	:5.4	:1.00	= 0.600600600E-03
:F6457	:7.2	:1.00	= 0.938438437E-03
:F6458	:5.5	:1.00	= 0.619369368E-03
:F6459	:7.5	:1.00	= 0.994744743E-03

:Q

SAMPLE #	RA 226 CT.	WET/DRY	RECOVERY	MICROCURIES/KG
:F6455	:225.8	:1.00	:0.656	= 0.758021291E-03
:F6456	:175.5	:1.00	:0.753	= 0.512875190E-03
:F6457	:0.300	:1.00	:0.687	= -0.964231633E-06
:F6458	:3.700	:1.00	:0.599	= 0.114275131E-04
:F6459	:66.30	:1.00	:0.723	= 0.200652202E-03

:Q

GAMMA CALIBRATION=: C/M/MICROCURIE.

GAMMA BKG=:

COMPTON BASELINE=:

SAMPLE #	GAMMA CT.	WET/DRY	GMS/VIAL	MICROCURIES/KG
:Q				

END OF JOB.

*

FIGURE 2. PRINTOUT OF TYPICAL RUN

"ALT MODE" in order to preserve the program format. The answers in microcuries per kilogram are typed out in floating point or exponential form since a wide range of values are possible and a loss of significant figures could result if a fixed point form were used.

The program is read in from paper tape once the FOCAL program is loaded and running. A GO command starts the program at the beginning. A GOTO 2.10 command starts the program at the total beta section. This GOTO command can be used to start the program at any subsequent section by typing the appropriate line number after the command.

In the event other factors are needed for which provision has not been made, the program can be modified after loading and a new tape can be punched if the change is to be permanent.

RESULTS AND CONCLUSIONS

A typical run of a set of samples is shown in Figure 2. This run was completed in about 10 min., a saving of about 50 min.

REFERENCES

1. Goldin, A. S., Anal. Chem., 33, 406 (1961).
2. McLane, C. K. and Peterson, S., "The Transuranium Elements," Seaborg, G. T., Katz, J. J., and Manning, W. M., NNS IV-14B Part II, McGraw-Hill Book Co., Inc., 1949, p. 1389.

A FOCAL COMPUTER PROGRAM FOR THE CALCULATION OF
PLUTONIUM-238/PLUTONIUM-239 RATIOS DETERMINED
BY ALPHA SPECTROMETRY

C. Zyskowski

In the isotopic analysis of plutonium by mass spectrometry,¹ traces of ²³⁸U in the plutonium fraction that survive the necessary separation step interfere with the determination of the ²³⁸Pu because of their identical mass. Reliance must be placed instead on the determination of ²³⁸Pu by alpha spectrometry,¹ a method made possible by the energy differences between the alpha particles of ²³⁸U and ²³⁸Pu. The necessary calculations can be carried out by means of a short computer program in the FOCAL language.

EXPERIMENTAL

Computer System. This FOCAL program was written for a Digital Equipment Corporation PDP-15 computer. It can also apply to the PDP-8 or PDP-9 computers.

Program. The equation for the determination of the ²³⁸Pu/²³⁹Pu atom ratio is as follows:¹

$$R_{8,9} = \frac{A_8 (3.708 \times 10^{-3}) (1 + [3.636] [R_{0,9}])}{A_{9,0}}$$

where $R_{8,9}$ = ²³⁸Pu/²³⁹Pu atom ratio,

$R_{0,9}$ = ²⁴⁰Pu/²³⁹Pu atom ratio as determined by mass spectrometry,

A_8 = integrated area under ²³⁸Pu peak,

and $A_{9,0}$ = integrated area under ²³⁹Pu, ²⁴⁰Pu peaks.

The constants are derived from the respective isotopic mass and half-life of ²³⁸Pu, ²³⁹Pu, and ²⁴⁰Pu.

On a WRITE command, the computer types the program listing including the line numbers and the indirect statements used as shown in Figure 1. After the program is read into the computer, the initial starting signal GO with a carriage return causes the printout of the program title and instructions to the operator. The operator then types the variables under the proper column headings: the sample number; the ²⁴⁰Pu atom ratio obtained from mass spectrometric data; and the ²³⁸Pu and ^{239,240}Pu peak activities determined from the alpha spectrometric data. The program supplies the constants automatically. FOCAL then types the answer

*WRITE ALL

C FOCAL15 V6A

```

01.04 T "    PROGRAM FOR PU 238/239 RATIO DETERMINATION.",!
01.05 T "    TYPE CTRL/P WHEN LAST SAMPLE IS FINISHED.",!!!!
01.10 SET A=.003708; SET B=3.636; SET R39=1
01.15 I "SAM. NO.      240/239 RATIO      238 ACT.      239 ACT.
01.16 T "238/239 RATIO",!!
01.20 ASK SAM
01.21 T "      "
01.25 ASK R40
01.26 I "      "
01.30 ASK A38
01.31 T "      "
01.35 ASK A39
01.36 T "      "
01.40 SET K1=B*R40
01.41 SET K2=K1+R39
01.42 SET K3=A38/A39
01.45 T % 9.09, A*K2*K3, '
01.50 GOTO 1.2, '

```

*

FIGURE 1 FOCAL PROGRAM LISTING.

*J0

PROGRAM FOR PU 238/239 RATIO DETERMINATION.
TYPE CTRL/P WHEN LAST SAMPLE IS FINISHED.

SAM. NO.	240/239 RATIO	238 ACT.	239 ACT.	238/239 RATIO
:PU 1561	:.093960	:1277	:16002	0.00039700
:PU 1562	:.094778	:1065	:13524	0.00039263
:PU 1565	:.093659	:1847	:22225	0.00041309
:PU 1566	:.094164	:2974	:36554	0.00040497
:PU 1572	:.094661	:5616	:70970	0.00039441
:TP				

FOCAL15 V6A
*

FIGURE 2 TYPICAL PROGRAM RUN FOR CALCULATION OF SEVERAL SAMPLES.

and remains in readiness for the next sample. Figure 2 shows a typical printout and user's responses to the program ASK commands, indicated by the colon character, for a series of samples. The user's responses are terminated by striking the ALT MODE key which tabs the carriage to the next column.

DISCUSSION

This program was originally designed for a more informal output format in which the requests for data were requested in clear text. However, it was decided that a tabular form of entry and response would be more neat and concise. One change that may be made in future work to benefit a user unfamiliar with computer operation concerns the initial instructions. This change will involve the use of the ALT MODE key on the teletype that will insert the data under the proper column headings.

REFERENCE

1. Pietri, C. E., Wenzel, A. W., Jasper, L. J., Jr., Finley, H. O., and Nelson, L. C., Jr., NBL-238 (May 1967) .

EVALUATION OF A COMMERCIAL GRAVIMETRIC PIPETTER FOR DISPENSING CONTROL STANDARD SOLUTIONS

L. J. Pinto and C. E. Pietri

The New Brunswick Laboratory (NBL) titrimetric method for the determination of uranium in uranium-plutonium¹ and other process samples² requires the use of control standards accurate to at least 0.03% (relative) of the actual quantity of uranium. Weight aliquots taken from standard solutions prepared on a weight basis from NBL dingot uranium metal are generally used. However, the customary procedure of weighing aliquots of the standard solutions by difference is tedious and time-consuming when literally hundreds of controls are required. Consequently, a simpler and faster method involving the use of a commercial gravimetric titrator³ to dispense weighed aliquots was evaluated.

EXPERIMENTAL

Reagents and Apparatus

Standard Uranium Solution, 0.02 g. U/g., prepared from NBL dingot uranium metal (99.972%) dissolved in 8N HNO₃. The solution is evaporated to a low volume to remove excess HNO₃ and then taken up to a known weight in a 2000-ml flask.

Test Tubes, 15 x 125 mm.

Gravimetric Titration Apparatus, Mettler DP-11, consisting of wind guard, ring platform, tubing holder with titrant flow valve and hand control, weight buret (polyethylene bottle) with 150-g maximum capacity, clip, buret tip which is lightly lubricated with silicone grease so that discrete drops of titrant will be dispensed, buret support and silicone rubber tubing. A Mettler Model P162 top-loading balance with a precision of 1 mg. is used to read the weight.

Procedure

Assemble the apparatus according to the manufacturer's instructions.³ Fill the buret about two-thirds full of the standard uranium solution. Without the wind guard in place, tighten the buret cap, open the hand control, gently squeeze the buret until several milliliters of solution pass from the tubing to remove any air bubbles. Close the hand control, loosen the cap to relieve the pressure, then release the buret. Put the wind guard in place. Adjust the sensitivity and re-adjust if necessary after 2 to 3 aliquots have been dispensed.

Adjust the balance to the weight of the desired aliquot, record the weight, and with a test tube under the buret tip, dispense about the desired weight, turn the weight control knob counter-clockwise

1 unit, touch off the buret tip, and record the final weight. Periodically recheck to see that there are no gas bubbles in the tubing or buret tip that would be dispensed with the solution. Remove bubbles as before, if necessary, and readjust the balance.

Repeat the aliquoting until the liquid level falls to the refill mark. Prepare each series of aliquots without interruption or refilling the buret. If a delay is necessary, dispense and discard a few milliliters before collecting the next aliquot. For each new series, refill the buret with standard solution, check the sensitivity and adjust if necessary. If the readings become erratic because of a build up of a static charge, wipe the wind guard with a damp cloth or immerse it in warm water.

RESULTS AND DISCUSSION

The apparatus was initially calibrated by dispensing water into small volumetric flasks and weighing the delivered quantity. This procedure was abandoned because of excessive error caused by evaporation during the delivery of the aliquot.

Calibration by dispensing a standard uranium solution was finally used because in this technique the evaporation problem did not exist and this type of solution was identical to that for which the apparatus was to be eventually used. This procedure is possible because the high-precision NBL titrimetric method involving the reduction to uranium(IV) by ferrous ion in phosphoric acid and titration with dichromate has been shown to give a precision (relative standard deviation) and accuracy (relative difference) of generally less than 0.05% with no bias.¹⁻³

About 180 aliquots of 1, 2, 5, and 10 g. each were delivered into test tubes and 7 to 9 tubes of each were then selected at random for analysis. In Table 1 the relative differences between the apparent weight of uranium dispensed and that found by analysis are listed for each size aliquot. It can be seen that the 10-g. aliquots are sufficiently precise and accurate to serve as control standards whereas the smaller aliquots are not. Although the manufacturer claims that the balance is precise to 1 mg., from this work the overall error in the system appears to be 3 to 4 mg. per aliquot.

One likely source of error was attributed to the formation of small bubbles in the rubber tubing connecting the buret and the dispensing tip. If bubbles in the tubing are present, positive or negative errors can result depending on whether the bubbles are near the buret being weighed or near the tip and being expelled.

Advantages of the dispensing apparatus over conventional weighing are speed, approximately 15 aliquots can be prepared per hour, and ease of operation. The buret does not have to be handled during the operation, the buret capacity is sufficient to provide a large number of aliquots in succession without refilling, and aliquots of identical weight can be dispensed. This latter factor can help speed up the necessary calculations. The apparatus will be studied in future work as a replacement for the conventional weight buret used in the NBL titrimetric determination of uranium in uranium-plutonium samples.

TABLE 1
THE RELIABILITY OF VARIOUS SIZE ALIQUOTS DISPENSED BY
THE METTLER DP-11 APPARATUS

	Relative Difference, %			
	1 g.	2 g.	5 g.	10 g.
	+ 0.162	- 0.082	+ 0.022	- 0.030
	- 0.198	- 0.046	+ 0.033	- 0.028
	- 0.102	+ 0.139	- 0.162	- 0.021
	- 0.084	+ 0.098	+ 0.089	+ 0.048
	- 0.059	- 0.143	- 0.044	+ 0.019
	+ 0.158	- 0.111	- 0.154	+ 0.058
	+ 0.212	- 0.153	- 0.014	- 0.009
				- 0.005
				+ 0.014
Relative Standard Deviation	0.16	0.12	0.09	0.03

ACKNOWLEDGMENT

The authors wish to thank A. R. Eberle of the Analytical Development Section and H. N. Simmons of the Plutonium Chemistry Section for their assistance in the titration of the uranium standards.

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3. Instruction Book, Mettler DP-11, Mettler Instrument Corporation, Princeton, N. J.
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CALIBRATION OF THE OAK RIDGE NATIONAL LABORATORY MODEL Q-1348C REMOTE PIPETTER FOR HOT CELL WORK

L. J. Pinto, C. E. Pietri, and E. H. Jacob

A remote pipetter for the precise and accurate delivery of volume aliquots of highly radioactive solutions is necessary for sampling and diluting in hot cell work. Several types of pipettors have been developed and are described in the literature.¹ Because of its reported ease of maintenance and high precision,² the Oak Ridge National Laboratory (ORNL) Model Q-1348C piston pipetter with a 1.2-ml. capacity was selected for use in the New Brunswick Laboratory (NBL) Hot Analytical Laboratory. This pipetter functions by controlling the distance a piston of known diameter moves in a chamber filled with sample solution. The volume delivered from the chamber is indicated by a dial on the control unit. A precision of 0.07% relative standard deviation (RSD) for the delivery of 0.1-ml. aliquots has been reported¹ for this model pipetter. In the present work, the precision and accuracy of dispensing various aliquots with the NBL instrument were determined.

EXPERIMENTAL

Apparatus

ORNL Model Q-1348C Remote Pipetter. The instrument, except for the graphite plunger and the fluorothene cylinder which were obtained from ORNL, was constructed in the NBL machine shop. The detailed operation of the pipetter, designed to deliver 0.1 to 1.0 ml., is described elsewhere.³

Procedure

Calibrate the pipetter by delivering the desired aliquots of water into tared weighing bottles and weighing the aliquot. Calculate the volume from the weight and density in the usual manner.

RESULTS AND DISCUSSION

For volumes of 0.1 to 0.5 ml., repetitive deliveries of the appropriate aliquot were made until the maximum number possible from the originally-filled pipet was reached. Thus, a series of ten 0.1 ml., five 0.2 ml., three 0.3 ml., two 0.4 or two 0.5 ml., was dispensed. Each series was then repeated from three to nine times to obtain sufficient data for statistical analyses. For aliquots of 0.6 to 1.0 ml. single deliveries were made from ten to fifteen times from a full pipet.

The statistical data are shown in Tables 1, 2, and 3.

TABLE 1

PRECISION AND ACCURACY OF VOLUMES DELIVERED AT SPECIFIC LEVELS OF PIPET

Aliquot Volume, ml.		Increment Delivered									
		1	2	3	4	5	6	7	8	9	10
0.1	RSD, % ^a	0.77	0.24	0.47	0.72	0.24	0.40	0.68	0.43	0.25	0.37
(N=6)	RD, % ^a	-0.90	-1.1	+0.60	-0.70	+0.30	+0.30	-0.10	0.00	-0.80	-1.4
0.2	RSD, %	0.37	0.34	0.27	0.24	0.49					
(N=9)	RD, %	-1.3	-0.50	-0.05	0.00	-0.95					
0.3	RSD, %	0.09	0.19	0.07							
(N=9)	RD, %	-0.33	+0.03	0.00							
0.4	RSD, %	0.03	0.10								
(N=7)	RD, %	-0.35	+0.38								
0.5	RSD, %	0.08	0.01								
(N=3)	RD, %	-0.10	+0.04								

a. RSD = relative standard deviation; RD = relative difference between actual and stated volume.

TABLE 2

PRECISION AND ACCURACY OF VOLUMES DELIVERED CONSECUTIVELY

Aliquot Volume, ml.		Series in Test								
		1	2	3	4	5	6	7	8	9
0.1 (N=10)	RSD, % ^a	0.92	0.89	0.75	0.84	0.72	0.74			
	RD, % ^a	-0.20	-0.50	-0.30	-0.10	-0.50	-0.60			
0.2 (N=5)	RSD, %	0.45	0.64	0.53	0.70	0.51	0.56	0.56	0.63	0.67
	RD, %	-0.15	-0.95	-0.95	-0.85	-0.35	-0.25	-0.35	-0.65	-0.60
0.3 (N=3)	RSD, %	0.17	0.21	0.25	0.25	0.20	0.22	0.18	0.28	0.32
	RD, %	-0.27	-0.17	-0.13	-0.03	0.00	-0.07	0.00	-0.07	-0.10
0.4 (N=2)	RSD, %	0.41	0.57	0.58	0.46	0.46	0.57	0.53		
	RD, %	0.00	+0.08	+0.10	-0.05	-0.05	+0.02	+0.05		
0.5 (N=2)	RSD, %	--	0.10	0.12	0.14					
	RD, %	--	+0.02	-0.04	-0.06					
0.6 (N=12)	RSD, %	0.06								
	RD, %	-0.03								
0.7 (N=10)	RSD, %	0.07								
	RD, %	+0.06								
0.8 (N=10)	RSD, %	0.10								
	RD, %	+0.18								
0.9 (N=10)	RSD, %	0.05								
	RD, %	+0.07								
1.0 (N=15)	RSD, %	0.08								
	RD, %	-0.02								

a. RSD = relative standard deviation; RD = relative difference between actual and stated volume.

TABLE 3

SUMMARY OF ALL DATA FOR ACCURACY AND PRECISION

<u>Aliquot Volume, ml</u>	<u>N</u>	<u>Average Volume Delivered, ml</u>	<u>RSD, %^a</u>	<u>RD, %^a</u>
0 1	60	0.0996	0.80	-0 40
0 2	45	0.1989	0.60	-0 55
0 3	26	0 2997	0 21	-0.10
0 4	14	0 4001	0.38	-0.02
0.5	6	0.4999	0 04	-0 02
0 6	12	0 5998	0 06	-0.03
0 7	10	0.7004	0 07	-0.06
0.8	10	0 8014	0 10	+0 17
0 9	10	0 9006	0.05	+0 07
1 0	15	0.9998	0.08	-0 02

a RSD = relative standard deviation

RD = relative difference between actual and
stated volume.

Table 1 summarizes the reliability of dispensing 0.1- to 0.5-ml. aliquots at specific levels of the pipet cylinder. Table 2 summarizes the reliability for these same volumes delivered consecutively plus that for 0.6- to 1.0-ml. volumes when the initial setting of the pipet control dial is zero. Table 3 presents the precision and accuracy of all the data accumulated.

As can be seen from Table 1 the reproducibility of delivery expressed as a relative standard deviation of an 0.1-ml aliquot from the same level of the pipet cylinder is not constant but ranges from 0.24 to 0.77% depending on the particular 0.1-ml aliquot delivered. For 0.2-ml aliquots, the range is 0 to 1.3%. For 0.3- to 0.5-ml. aliquots, the precision improves somewhat, but only the 0.5-ml. deliveries are within 0.10%. When one considers the consecutive delivery of the same aliquot as is summarized in Table 2, again the relative standard deviation of the volumes delivered are poor for the 0.1- to 0.4-ml. aliquots and acceptable for the 0.5-ml. and also for 0.6- to 1.0-ml. aliquots.

The accuracies are expressed as the relative difference (RD) from the stated value. These data and the precision data are summarized in Table 3. For the 0.1- and 0.2-ml. aliquots the accuracy of delivery is unacceptable, whereas, for the 0.3- to 1.0-ml aliquots, with the exception of the 0.8-ml aliquot, it is satisfactory. A correction factor presumably can be applied to the 0.8-ml aliquot because of the satisfactory precision.

On the basis of both the precision and accuracy values obtained, the pipetter appears to be useful chiefly for 0.5- to 1.0-ml. volume aliquots. The reason for the unreliability of delivery of the smaller aliquots will be sought in future work as time permits.

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