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**ANNUAL PROGRESS REPORT FOR THE
PERIOD JULY 1968 THROUGH JUNE 1969**

April 1970

New Brunswick Laboratory (AEC)
New Brunswick, New Jersey

UNITED STATES ATOMIC ENERGY COMMISSION • DIVISION OF TECHNICAL INFORMATION

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UNITED STATES ATOMIC ENERGY COMMISSION

ANNUAL PROGRESS REPORT FOR THE PERIOD
JULY 1968 THROUGH JUNE 1969

AEC Research and Development Report

C. J. Rodden, Director

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April 1970

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ABSTRACTS

Titrimetric Determination of Uranium in Product, Fuel and Scrap Materials After Ferrous Ion Reduction in Phosphoric Acid: Manual and Automatic Titration

Improved procedures for determining uranium by ferrous reduction in phosphoric acid and titration with dichromate are presented. Applications of the procedures to the analysis of many materials in the uranium fuel cycle are described. Precisions and accuracies are well within 0.1%, and the analysis times are greatly reduced. Automation of the basic procedure has been successful.

Rapid Separation of Uranium by Reversed-Phase Chromatography and Measurement by Oxidimetric Titration After Ferrous Reduction in Phosphoric Acid

A method for determining uranium involving separation by reversed-phase chromatography and a titrimetric measurement after reduction by ferrous ion in phosphoric acid is described. The prior column separation technique has the advantages of concentrating the uranium, of removing some interferences and of presenting the possibility of decontaminating spent fuel solutions.

Recovery of Uranium from Phosphoric Acid Solutions

Enriched uranium can be recovered in a novel way from phosphoric acid solutions by first extracting the phosphoric acid with n-butyl alcohol. The raffinate is then extracted with tributyl phosphate, and the uranium is stripped from the organic phase and precipitated. With two such recovery steps, 85 to 90% of the uranium is recovered as 95 to 98% pure U_3O_8 .

Determination of Uranium After Reduction with Ferrous Ion in Phosphoric Acid; Titration with Vanadate

Vanadium oxide can be used as a standard to prepare sodium vanadate solutions for titration of reduced uranium. The vanadium in the titrant sharpens the endpoint, and obviates the need for adding vanadium(IV) ion before titration after ferrous reduction in strong phosphoric acid. A vanadium oxide purity of 99.94% was obtained with a volumetric-potentiometric titration.

X-Ray Spectrographic Determination of Uranium in Uranium-Zirconium Solutions - A Progress Report

An X-ray spectrographic procedure is described for the determination of uranium in uranium-zirconium solutions. A bismuth internal standard is used.

Automatic Determination of Uranium with the Technicon Autoanalyzer - A Progress Report

A system was devised which permits the automatic analysis of uranium in nitric acid solutions with the Technicon Autoanalyzer in the 0.5 to 10 $\mu\text{g./ml.}$ range. The method consists of a TBP extraction followed by the stripping of the uranium from the TBP phase with a buffer solution of the chromogenic reagent, Arsenazo III.

Estimation of Gamma-Ray Self Absorption Coefficient in the Determination of Uranium-235 in Solid Samples

The self absorption coefficient needed in the determination of uranium-235 in solid samples by gamma counting was estimated by counting several sample aliquots differing in weight and applying a computer program to calculate the least square analysis of the self absorption curve.

Controlled Potential Coulometric Determination of Plutonium

Reliable results were obtained in the determination of plutonium by controlled potential coulometry at a platinum electrode by adopting a consistent pretreatment of the solutions before titration.

A Ten-Year Evaluation of the Stability of Plutonium Sulfate Tetrahydrate

The stability of plutonium sulfate tetrahydrate, a proposed primary standard for plutonium, has been evaluated periodically for 10 years.

The Effect of Exposure of Plutonium Sulfate Tetrahydrate to Environments with Extreme Humidities

An investigation was made into the effect on plutonium sulfate tetrahydrate of exposure to high humidity, 95% relative humidity, (R.H.), followed by drying at 40% R.H. and at < 0.1% R.H., and of exposure to low humidity, < 0.1% R.H., after storage in the stable 17 to 75% R.H. range. No apparent permanent effect on the plutonium content of the compound was found after re-equilibration at 40% R. H.

Determination of Plutonium by Isotope Dilution Mass Spectrometry. I. Effect of Variation of Tracer to Sample Ratio

In the determination of plutonium in dissolver-type solutions by isotope dilution mass spectrometry, the reliability of measurements was determined for ratios of Pu^{242} tracer to Pu^{239} sample of 1:2 and 2:1.

The Determination of Uranium in Uranium-Plutonium Mixtures by Ferrous Reduction in Phosphoric Acid and Potassium Dichromate Titration: An Evaluation

The determination of uranium by ferrous reduction in phosphoric acid and potassium dichromate titration was evaluated more fully using uranium-plutonium solutions with a 20% plutonium content. Plutonium did not interfere at this concentration.

Improvements in the method were made in order to avoid precipitation of plutonium. The effect of americium as a possible interference was studied and found to be insignificant. Indicator versus potentiometric endpoint detection was compared and coefficients of variation of 0.06% and 0.03%, respectively, were found.

Determination of Carbon in Boron and Boron Carbide

A method for determining carbon in boron using a high frequency induction furnace and a gas chromatograph is described. Comparative results obtained by the induction heating method and the peroxide fusion method are presented.

Preparation of Boron-Filled Silicone Elastomer for Emission Spectrographic Analysis

A method is described for the determination of impurities in boron-filled elastomers by preconcentration and incorporation of the impurities into a gallium oxide matrix. The effect of the large quantities of beryllium present in the samples on the chromium results was studied.

Analysis of Silicone Elastomers by Atomic Absorption Spectroscopy

The analysis of silicone elastomers by atomic absorption spectroscopy requires the destruction of the organic matter, removal of the large concentrations of silica and concentration of the impurities. Such a dissolution procedure was used in the impurity analysis of several samples on which comparative results obtained by emission spectroscopy were also determined.

Getter System for Impulse Heater Gloved Box

A gas purifying and recirculation system designed to remove water, carbon dioxide, and oxygen from the helium atmosphere in the impulse heater gloved box is described.

A Computer Controlled Isotope Ratio Mass Spectrometer with Dry Reed Relays

A computer controlled data acquisition system for mass spectrometric isotopic analysis of uranium and boron is briefly described.

A Symmetrical Cylindrical Rotating Step Sector

A new symmetrical cylindrical rotating step sector was designed and constructed.

A Darkroom Timer

A reliable electromechanical darkroom timer is described. The timer automatically resets for use in total darkness and the timing cycle can be changed by switching for time differences between development and fixing of film and plates.

TITRIMETRIC DETERMINATION OF URANIUM IN PRODUCT,
FUEL AND SCRAP MATERIALS AFTER FERROUS ION
REDUCTION IN PHOSPHORIC ACID: MANUAL AND
AUTOMATIC TITRATION

A.R. Eberle, M.W. Lerner, C.G. Goldbeck, and C.J. Rodden

The titrimetric method of determining uranium involving reduction to uranium(IV) by iron(II) in phosphoric acid, selective oxidation of the excess iron(II) and titration with dichromate has enormous potential to satisfy the burgeoning demand for faster and cheaper yet reliable uranium analyses required for the safeguard program. The method requires no prior separations even in the presence of iron, nitrate, plutonium, and other elements normally interfering with conventional redox methods. In the present work significant improvements have been made that greatly increase the versatility and reliability of the method. The introduction of vanadium(IV) to the solution being titrated has dramatically sharpened the endpoint so that potentiometric titration can be used. Conditions have been found that permit large sample volumes to be analyzed. Studies of other parameters have been made.

The proposed method can be used for virtually every step in the uranium fuel cycle. Analyses are reported of synthetic and actual sample solutions of product material, fuels of various types including mixtures of uranium with plutonium, zirconium, zircaloy, thorium, stainless steel, aluminum, beryllium, and niobium, fuel scrap materials including dissolver solutions of many types and residue samples. Dissolution procedures for a wide variety of solid samples are presented. Actual analysis time for typical sample solutions has been lowered from about 3 to 4 hr. (2 days elapsed time) for conventional methods down to less than 15 min. (1 hr. elapsed time if an evaporation step is needed) for the recommended method. The accuracy and precision of results are also better, generally being well within 0.1%.

The method is particularly attractive for automation because all operations are carried out in the same beaker and the reagent additions are generally not critical. Automatic titration was accomplished by the use of a timer-controller plus a basic commercial titrator that requires only simple modifications. Twelve samples can be analyzed within 3 hr. with the proposed instrument. The reliability of the automatic titration appears to be only slightly less than obtained with manual titration.

A complete report of this work will be published elsewhere.

RAPID SEPARATION OF URANIUM BY REVERSED-PHASE CHROMATOGRAPHY AND MEASUREMENT BY OXIDIMETRIC TITRATION AFTER FERROUS REDUCTION IN PHOSPHORIC ACID

C. E. Hedrick and M. W. Lerner

A titrimetric method^{1,2} of determining uranium involving the reduction of uranium(VI) to uranium(IV) by iron(II) in strong phosphoric acid, selective oxidation of the excess iron(II) by nitric acid and molybdate catalyst, and titration of the uranium(IV) with dichromate has recently been evaluated at the New Brunswick Laboratory (NBL).³ A large number of uranium fuel and scrap sample solutions were analyzed and a slightly improved procedure was reported.

At that time several factors still limited the enormous potential of the method. The endpoint in the titration was sluggish despite the improvement gained by diluting the reduced solution to twice the suggested volume before titration.³ The endpoint was particularly poor when fluoride ions were present. Subsequent work⁴ at NBL dramatically sharpened the endpoint by the addition of vanadyl ions to the solution being titrated.

Yet other disadvantages remained. In addition to the known interferences of molybdenum plus nitric acid, halogens, silver(I) and tin(II), manganese was found to give serious negative errors. Lastly, the limitation of a sample solution volume of 15 ml. or less was a serious disadvantage in the analyses of dilute solutions that could not be concentrated by evaporation because of solids deposition.

Hamlin and coworkers⁵ have shown that columns of porous fluorocarbon loaded with tri-n-butyl phosphate (TBP) efficiently extract uranium(VI) from nitrate solutions. In the present work, this technique is refined by using a highly efficient salting solution, a hot stripping solution, and a modified column design to collect and recover the uranium quantitatively. The use of this improved procedure together with the modified oxidimetric titration method similar to that in reference (4) permits the preconcentration and determination of uranium from a wide variety of alloy and process solutions. Although many of the samples tested can be analyzed directly, the prior column separation technique has the advantages of concentrating the uranium, of removing some interferences, and of presenting the possibility of decontaminating spent fuel solutions from certain highly radioactive fission products.

Experimental

Reagents and Apparatus

Salting Solution, prepared by adding 900 g. of aluminum

nitrate nonahydrate and 900 g. of sodium nitrate to 1700 ml. of hot water, 25 ml. of HNO_3 and 50 ml. of TBP, and stirring the mixture. The lower phase is used for both sample treatment and column washing.

Stripping Solution, prepared in small batches by adding 25 ml. of H_2SO_4 to a mixture of 100 ml. of 30% hydrogen peroxide and 400 ml. of water. A quantity is heated to near boiling before use.

Reduction, Oxidation, and Titration Reagents. Reagents for the preliminary reduction procedure include 85% H_3PO_4 , 15% sulfamic acid, and 1M ferrous sulfate in 5% H_2SO_4 . The catalytic oxidizing solution is prepared by dissolving 4 g. of ammonium molybdate in 200 ml. of water, adding 300 ml. of 15% sulfamic acid and 500 ml. of HNO_3 . The titrant is 0.02N ceric sulfate solution prepared by diluting 0.1N reagent solution (G. F. Smith Chemical Company) with cold 5% H_2SO_4 and standardizing against standard uranium solution by the proposed method. The accelerator solution is prepared by dissolving 20 g. of vanadyl sulfate dihydrate and 20 ml. of H_2SO_4 in 1 liter of water. The indicator solution is prepared by dissolving 1 g. of 4,7-dimethyl-1,10-phenanthroline hydrate (G. F. Smith Chemical Company) in 10 ml. of glacial acetic acid, adding water containing the theoretical quantity, 0.41 g., of ferrous sulfate heptahydrate needed to complex the indicator base, and diluting to 500 ml.

Standard Uranium Solution, prepared by dissolving NBL standard dingot metal (99.972% U) in HNO_3 and diluting to an appropriate volume.

Columns are 1-x15-cm. pyrex tubes equipped with teflon stopcocks and 40-ml. reservoirs. Packing is a porous fluorocarbon, 80 to 90 mesh, obtained from Analytical Engineering Laboratories, Hamden, Connecticut. Columns are packed in two steps. In the first step, diethylether is used to dampen dry support, a portion of which is then slurried with water and added to the column plugged with the minimum quantity of glass wool. This layer is packed by water elution to a depth of about 2 cm. In the second step, the upper 10-cm. portion of the column is packed with a water slurry of 25% by volume TBP-support mixture. The top of the column is covered with another small layer of glass wool to prevent column breakup during the stripping operation. The column is normally operated with mild suction to increase the flow rate.

Procedure

Add three times the volume of salting solution to a 50-ml. volume of uranium(VI) sample solution containing less than 50% by volume of free mineral acid. Pass the mixture through the column at about 3 ml. per min. using suction if necessary. Wash the uranium band with 25 to 50 ml. of salting solution previously used to rinse out the sample beakers. Wash out the uranium with 150 ml. of stripping solution heated to 90°C.

Evaporate the uranium solution to a volume less than 25 ml. in a 800-ml. beaker covered with a smooth watch glass. Cool. Wash down the watch glass and beaker sides with 5 ml. of water and 5 ml. of sulfamic acid solution with a pipet. Add 50 ml. of H_3PO_4 . Add 5 ml. of the ferrous sulfate solution with swirling. After

1 min. wash down the sides of the beaker using 10 ml. of the HNO_3 -molybdate solution, swirling after the addition. About 3 min. after the solution clears, add a solution of 25 ml. of H_2SO_4 and 350 ml. of water plus a stirring bar. Begin the stirring and add 10 ml. of the vanadyl solution and 1.0 ml. of the indicator solution. Titrate with the ceric sulfate titrant to the indicator endpoint, the change from a red to sky-blue.

Determine a blank by analyzing two aliquots of the sample, one aliquot being two times as large as the other as described previously.³ Alternatively, determine the reagent blank directly by analyzing a solution containing no uranium.

Results and Discussion

The extraction of uranium(VI) by reversed-phase chromatography is advantageous because even those impurities with relatively high distribution ratios can be separated from the uranium. For example, the theoretical volume necessary to elute a substance from a solvent-loaded column follows the equation:

$$V_R = V_M + DV_S$$

where V_R is the retention volume of the solute peak, V_M is the volume of mobile phase in the column, D is the batch distribution ratio and V_S is the volume of stationary phase. The quantity V_M can be approximated to be about half the total column volume, and V_S is estimated from the volume of solvent on the support. A substance with a D of 5 (about 83% extracted), therefore, is seen to be eluted completely from a 12-cm. column with about 50 ml. of wash solution.

Table 1 includes the elements that may co-extract with the uranium. The distribution ratios were obtained by conventional 1-min. batch equilibrations using separatory funnels followed by analysis of the aqueous phase. Most of these elements do not interfere in the titrimetric measurement. In the separation procedure, thorium is a potentially serious interference in large amounts because it may saturate the column and prevent the quantitative extraction of uranium. With much thorium present, the sharp uranium band becomes much wider. The use of a saturated sodium nitrate solution instead of the proposed salting solution moderates this effect somewhat. Molybdenum(VI) as such or as a heteropoly acid strongly coextracts and is not quantitatively eluted. The portion eluted may cause low results in the titration by pre-catalyzing the oxidation of the reducing iron(II). Cerium(IV), chromium(VI), and manganese(VII) are not retained when the sample solution is treated with sodium bisulfite prior to the column separation. If not reduced, large amounts of cerium(IV) and chromium(VI) may disturb the uranium extraction; manganese(VII) is reduced to the dioxide on the column and is partially eluted with the uranium to cause negative errors in the titration.

Although vanadium can be tolerated to a large extent in the direct titration procedure by increasing the catalytic oxidation time,³ large amounts of chromium, and manganese in smaller quantities interfere in one way or another. The intense color of green chromium(III) ion, for example from stainless steel samples, obscures the indicator endpoint. Manganese gives low results by

TABLE 1

DISTRIBUTION RATIOS OF SELECTED METAL IONS BETWEEN
SALTING SOLUTION AND TRIBUTYL PHOSPHATE

<u>Metal Ion</u>	<u>D</u>	<u>Analytical Method</u>
U(VI)	4300	Fluorescence
Th(IV)	930	Gravimetric, ThO ₂
Zr(IV)	6.3	Gravimetric, ZrP ₂ O ₇
Sn(IV)	36	Gravimetric, SnO ₂
Mo(VI)	136	Spectrophotometric ^a
Fe(III)	0.93	Redox Titration
Au(III)	480	Gravimetric, Au
Ag(I)	0.02	Volumetric, KSCN
Cu(II)	1.8	Volumetric, I ₂
Cr(VI)	1.6	Redox Titration
Ce(IV)	69	Redox Titration
Mn(VII)	16.3	Redox Titration
Hg(II)	4.9	Volumetric, KSCN

a. Analysis of TBP at 430 m μ .

some mechanism that is not clear at present. The effect of manganese can be decreased by shortening the oxidation time. Thus, with both manganese and vanadium present, the errors cannot be reduced to negligible values by the oxidation timing since the beneficial effects are in opposite directions. The column separation technique is helpful, then, with this type of sample.

Considerable difficulty was initially encountered in removing the last 1% of the uranium from the column. The error persisted even though the column was washed before use with 1M sodium hydroxide to remove butyl phosphoric acids which have high distribution ratios for uranium. The error was finally categorized as: (1) loss of micro-droplets of solvent from columns without the underlayer of subsaturated support; (2) retention of uranium as a co-extracted molybdenum compound; (3) losses of uranium(IV) with solutions that were not pre-oxidized; and (4) losses of uranium resulting from diffusion into the inner portions of support grains. Errors caused by the last difficulty were reduced considerably by using a large volume of hot stripping solution. Column design, the use of peroxide in the stripping solution to break up molybdenum compounds, and the pre-oxidation of uranium(IV) to uranium(VI) in the sample solutions corrected the other difficulties. The stated volume of 50 ml. of sample solution can be increased to at least 250 ml. but the elution times then become lengthy.

The use of ceric sulfate as the titrant and 4,7-dimethyl ferroin indicator instead of the usual dichromate-barium diphenylamine sulfonate system³ was chiefly a matter of choice. It was felt desirable to be able to determine a direct blank; this determination cannot be done with the latter system.

With the quantity of H_3PO_4 used in the reduction, an initial sample size of up to 25 ml. can be used in contrast to the upper limit of 15 ml. in the original procedure.

Table 2 indicates the types of process samples often encountered in nuclear fuel analysis to which the proposed method has been applied. Very dilute solutions and stainless steel samples containing vanadium and manganese are included. Not tested was the decontamination ability of the column technique but it is known that many fission products present in spent fuels will not extract.

ACKNOWLEDGMENT

We wish to thank Alan R. Eberle for his general advice in the course of this work.

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TABLE 2

ANALYTICAL RESULTS OBTAINED BY THE PROPOSED PROCEDURE

Sample Solution	Uranium, %		Relative Difference, %	Relative Standard Deviation, %	N
	Present ^b	Found			
U-Fe ^a	5.559	5.556	-0.017	0.07	4
U-Stainless Steel ^a	0.7973	0.7986	+0.16	0.13	4
U-Stainless Steel ^a	0.09800	0.09778	-0.08	0.31	3
U-Stainless Steel (NBS-160a) ^a	0.4683	0.4692	+0.19	0.14	4
U-Zircaloy ^a	0.4923	0.4916	-0.14	0.07	2
U-Zircaloy ^a	2.513	2.515	+0.08	0.12	4
U-Zircaloy ^a	0.3274	0.3272	-0.06	0.17	3
U-Zr	0.027	0.0308	+14.1	0.65	4
U-Nb-Cr	0.059	0.05758	-2.41	0.90	2
U-Nb-Cr	0.117	0.1179	+0.77	0.37	2
U-Nb-Cr	0.426	0.4284	+0.56	0.08	2
U-Al-Zr ^a	0.0200	0.01995	-0.25	1.75	2
U-Al-Zr ^a	0.0349	0.0346	-0.85	0.55	2
U-Al-Zr ^a	0.0786	0.0779	-0.90	0.89	2
U-Al-Zr ^a	0.0996	0.0991	-0.50	0.10	2
UO ₂ (NO ₃) ₂ ^{a, c}	0.01535	0.01521	-1.56	1.06	2
UO ₂ (NO ₃) ₂ ^{a, c}	0.00413	0.00412	-0.24	0.72	2

a. Synthetic solution; all others actual samples.

b. Added quantity in synthetic solutions; in others, quantity found by conventional method involving sulfide and cupferron precipitation, Jones reductor, titration with potassium dichromate and barium diphenylamine sulfonate indicator.

c. Sample volume of 100 ml. before salting instead of 50 ml.

RECOVERY OF URANIUM FROM PHOSPHORIC ACID SOLUTIONS

C. E. Hedrick

Many processes have been described for the recovery of uranium from phosphate solutions. These methods are generally expensive but the expense is justified if enriched uranium is to be recovered.

Clegg and Foley¹ have summarized the important methods developed prior to 1958. They include: (1) reduction to uranium(IV) with iron, extraction with nonyl pyrophosphate and precipitation as the tetrafluoride; (2) direct precipitation of uranium(VI) phosphate from monosodium phosphate solution; (3) extraction from nitric-phosphoric acid solution with tributyl phosphate (TBP) and precipitation as ammonium diuranate.

Bailes and coworkers explored many approaches leading to a patent² involving the reduction to uranium(IV), precipitation with fluoride and leaching of the collected precipitate. Other precipitation methods have been recommended: precipitation as phosphates;^{3,4} reduction with iron followed by treatment with ammonia;⁵ precipitation with antimony trioxide;⁶ prior removal of several elements by alkali precipitation at pH 4.0 followed by sulfite reduction of uranium and precipitation of uranium(IV) phosphate.⁷

An electrolytic method based upon the electrolysis of a monocalcium phosphate solution and the collection of the uranium on the cathode has been described.⁸

Anion exchange resin separations have been recommended.^{9,10}

Numerous extraction processes have been reported. Dibutyl carbitol extracts uranium from phosphate solution salted with aluminum, copper, or ferric nitrate.¹¹ Bailes and Long¹² used alkyl phosphates, phosphonates and phosphites to extract uranium reduced with aluminum or iron powder. The same authors¹³ also described a method involving the extraction with octyl pyrophosphate in hexane. Russian workers¹⁴ have used alkyl pyrophosphates. The synergistic effect of mixtures of alkylated phosphorus-containing solvents has been utilized to extract uranium from phosphoric acid solutions.¹⁵⁻¹⁷ These extractants are generally costly. Reversed-phase chromatography¹⁸ separates uranium but the capacity of the silica gel columns used are low.

In the present work, an efficient yet relatively inexpensive method for recovering enriched uranium from analytical solutions was sought. A different approach was used: the prior separation of the phosphoric acid. The proposed method involves the extraction of the phosphoric acid with n-butanol. The uranium is

then extracted from the raffinate with TBP, is stripped from the TBP and precipitated with ammonia.

Experimental

Reagents

n-Butyl Alcohol.

Sodium Sulfate, anhydrous.

Methyl Orange, 0.1% - phenolphthalein, 0.1% in isopropyl alcohol.

Tributyl Phosphate, washed well with sodium hydroxide solution and water.

Sodium Hydroxide Solution, 1M.

Ammonium Hydroxide, carbonate-free, prepared from tank ammonia.

Procedure

Adjust the sample solution with water or H_2SO_4 to a total strong acid acidity between 3 and 6N after a prior titration of a sample with sodium hydroxide solution to a methyl orange endpoint. Add 25% (w/v) anhydrous sodium sulfate to the solution. Extract 5X with an equal volume of anhydrous n-butyl alcohol. Add 2 vol. % of H_2SO_4 and 15 vol. % of water after each extraction. Reserve the combined organic phase.

Add an equal volume of HCl to the aqueous phase. Filter the precipitated sodium chloride on a fritted-glass funnel and wash with 8M HCl. Extract the filtrate and wash with an equal volume of TBP. Wash the organic phase twice with an equal volume of 8M HNO_3 . Discard the washes.

Strip the uranium from the TBP phase with two equal volume washes of water at 70°C followed by two equal volume washes of saturated ammonium carbonate solution at 70°C . Combine the washings and acidify carefully with HCl. Filter the solution through wet paper to remove residual TBP. Boil the solution to remove carbon dioxide and precipitate the uranium with ammonium hydroxide in the presence of filter pulp. Ignite the precipitate to U_3O_8 .

To recover the uranium partially extracted in the H_3PO_4 extractions, dilute the recovered H_3PO_4 , after distilling the butanol, to 40% with water, add 25% (w/v) anhydrous sodium sulfate and extract 5X with n-butanol as before. Recover the uranium in the raffinate by adding a small amount of solid ammonium persulfate and boiling the solution, cooling, adding an equal amount of HNO_3 and extracting with an equal volume of TBP. Backwash the organic phase once with 8M HNO_3 discarding the wash, then strip and precipitate the uranium as described above.

Results and Discussion

Extraction of H_3PO_4 . Several solvents were tested for their ability to extract H_3PO_4 from solution in the presence and absence of salts, Table 1. The data show that isopropyl alcohol is the most efficient among those tested, but it requires an aqueous phase saturated with sodium chloride. Other disadvantages with this system are precipitation of sodium chloride after equilibration, the large volume change of about 30% on equilibration, and the impossibility of a second equilibration with fresh isopropyl alcohol because of the appearance of a single phase at this point.

A better extractant was found to be n-butyl alcohol used in conjunction with added H_2SO_4 and sodium sulfate, Table 2. It can be seen that the best results, considering both extraction and volume changes, are obtained when the strong acid concentration including the first hydrogen of H_3PO_4 is adjusted between 3 and 6N. This acidity can be determined by titration with 1M sodium hydroxide and a mixed indicator composed of methyl orange and phenolphthalein. The volume of titrant up to the methyl orange endpoint (red to yellow) represents the sum of the mineral acid and H_3PO_4 in the aliquot analyzed. (The volume of titrant between the methyl orange endpoint and the phenolphthalein endpoint represents the H_3PO_4 only.)

Single batch extractions indicate that the H_3PO_4 has a distribution ratio of 0.65 in the proposed system. In Table 3, the results for N number of extractions are calculated using this value for the distribution ratio. In actual practice, the distribution ratio determined for the H_3PO_4 based upon a 5-stage extraction is higher, 0.94, because partially preequilibrated systems are used after the first stage, and because the H_3PO_4 and H_2SO_4 concentration changes at each stage affect the ratio. Table 3 presents data based upon both D values.

Extraction of Uranium. Uranium recovery studies with the systems shown in Table 2 indicated that up to 60% of the uranium extracts along with the H_3PO_4 in the absence of sodium sulfate. The addition of HF does not improve the uranium recoveries. In the absence of sodium sulfate, uranium is also lost by entrainment as seen by the formation of a haze in the butanol layer. In the presence of the sodium sulfate, 90% of the uranium is present in the raffinate after the five extractions of the H_3PO_4 . The measured distribution ratio based on the five-stage extraction is thus 0.022 as indicated in Table 3.

Extraction of Other Substances. Molybdenum(VI) is quantitatively extracted along with the H_3PO_4 . Iron(III) is only slightly extracted. Chromium(III) and vanadium(IV) are not extracted. Monobasic acids such as HCl, HNO_3 , and HF are extracted as well or better than the H_3PO_4 . Sulfuric acid is not well extracted. The behavior of other elements was not studied.

Recovery of Uranium. Analytical uranium-bearing H_3PO_4 solutions frequently contain iron, zirconium, or thorium. These elements, which presumably would not extract to a great extent and would accompany the uranium in any basic precipitation step carried out on the raffinate, are separated from the uranium by a TBP extraction step. An HCl system separates uranium from

TABLE 1

EXPLORATORY SOLVENT EXTRACTION STUDIES

<u>Solvent</u>	<u>Aqueous Phase</u>	<u>Distribution Ratio</u>	
		<u>H₃PO₄</u>	<u>Mineral Acid</u>
2-methylhexanone	H ₂ O-H ₃ PO ₄	0.0076	--
n-pentyl alcohol	H ₂ O-H ₃ PO ₄	0.27	--
isopropyl alcohol	Sat. NaCl-H ₃ PO ₄	2.6	2.5
n-butyl alcohol	H ₂ O-H ₃ PO ₄	0.57	--
n-butyl alcohol	Sat. NaCl-H ₃ PO ₄	0.42	0.11
n-butyl alcohol	10% H ₂ SO ₄ -Sat. NaCl-H ₃ PO ₄	0.8	1.1

zirconium and thorium better than a HNO₃ system.¹⁹ Washing the TBP extract with 8M HNO₃ removes coextracted iron(III).

The 10% loss of uranium occurring by extraction along with the H₃PO₄ is recovered after a second five-stage extraction of the H₃PO₄. This step is carried out by distilling off the butanol after the first extractions, diluting the residue to 40% with water and extracting five more times, and extracting the raffinate again with TBP. In this case, however, the uranium is already free of most metal contamination and an 8M HNO₃ system can be used directly with one 8M HNO₃ backwash. Table 4 presents the recoveries obtained from 40% H₃PO₄ solutions, and from 3M H₃PO₄ solutions containing large amounts of HNO₃, H₂SO₄, iron(III), chromium(III), molybdenum(VI), and vanadium(IV) as obtained by analyzing simple uranium solutions by the titrimetric method involving the reduction of uranium by iron(II) in H₃PO₄. Total uranium recoveries range from 80 to 89%. With the 40% H₃PO₄ solutions, the recovery apparently depends on the quantity of uranium present, but the lower limit by extrapolation is about 79%.

The purity of the U₃O₈, as determined by analysis, averages 96% for the first five-stage extraction step and 85.9% for the second. These oxides apparently contain some pyrophosphate: a pure uranyl pyrophosphate assays 85.8% pure as oxide.

Conclusions

The proposed process can recover nearly 90% of enriched uranium from solutions containing high concentrations of H₃PO₄. In the process the H₃PO₄ and n-butanol extractant can also be easily recovered. On this basis, and considering the low cost of butanol, sodium sulfate and TBP, the method is relatively inexpensive; however, actual cost estimates have not been made. The method is relatively simple and convenient.

TABLE 2
EXTRACTIONS WITH n-BUTYL ALCOHOL

Aqueous Phase	Temp., °C	Initial Conc. M ^a		Total H Conc.	Extraction, Mole %		Volume Ratio Change Va/Vo	Distribution Ratio of P, D ^b
		P	H		P	Extra H		
H ₃ PO ₄	27	0.60	-	0.60	16.8	-	0.80	0.16
		1.50	-	1.50	18.3	-	0.80	0.23
		2.92	-	2.92	29.5	-	0.74	0.31
		4.44	-	4.44	40.6	-	0.56	0.38
		5.80	-	5.80	63.9	-	0.33	0.58
		7.04	-	7.04	miscible	-	-	-
H ₃ PO ₄ -H ₂ SO ₄	25	1.40	0.39	2.18	18.2	25.0	0.80	0.18
		1.49	0.66	2.81	34.6	19.6	0.75	0.40
		1.30	1.10	3.50	29.4	23.2	0.73	0.31
		1.20	1.62	4.44	34.5	31.0	0.67	0.34
		1.26	2.23	5.72	39.6	42.2	0.56	0.37
		1.16	2.62	6.40	51.2	46.2	0.49	0.51
		1.16	3.72	8.60	85.0	83.0	0.14	0.75
25% Na ₂ SO ₄ -H ₃ PO ₄ -H ₂ SO ₄	22	2.80	1.67	6.13	46.6	16.0	0.75	0.65
HNO ₃	24	-	1.42	1.42	-	47.2	0.82	-
HCl	24	-	1.06	1.06	-	29.0	0.75	-
HF	26	-	0.16	0.16	-	62.8	0.80	-
		-	1.03	1.03	-	46.5	0.77	-
		-	2.69	2.69	-	47.0	0.72	-

a. H refers to mineral acid, P to H₃PO₄, M to molar concentrations.

b. Distribution ratio, D = (% extracted/100-% extracted) (Va/Vo).

TABLE 3

EXTRACTION OF PHOSPHORIC ACID AND URANIUM AS A
FUNCTION OF NUMBER OF EXTRACTIONS

Number of Extractions, N	H ₃ PO ₄ Extracted, Mole %		Uranium Recoverable, Wt. % ^c
	Calculated ^a	Actual ^b	
1	39.4	51.8	97.8
2	63.2	73.4	95.9
3	77.3	86.3	93.7
4	86.5	92.9	91.8
5	91.8	97.4	90.0
6	95.0	98.1	87.9
7	97.0	99.0	85.9
8	98.2	99.5	84.1
9	98.9	99.8	82.2
10	99.1	99.9	80.1

a. Based on single equilibration D of 0.65.

b. Based on 5-extraction measured D of 0.94.

c. Based on 5-extraction measured D of 0.022.

TABLE 4

RECOVERY OF URANIUM FROM PHOSPHORIC ACID SOLUTIONS

Aqueous Phase	Uranium Present, mg.	Uranium Recovered, %		Total Recovery, %	Oxide Purity, % ^a	
		1	2		1	2
40% H ₃ PO ₄	663.2	82.2	6.8	89.0	97.5	94.5
	514.7	77.3	7.9	85.2	87.6	84.5
	211.8	76.6	4.8	81.4	96.7	81.2
	86.4	73.2	7.0	80.2	97.4	74.7
3M H ₃ PO ₄ ^b	716.2	79.6	7.1	86.7	99.5	96.4
	226.5	80.5	6.4	86.9	97.1	84.2
Average		78.2	6.7	84.9	96.0	85.9

a. Two five-stage extractions.

b. Waste solution obtained by analyzing uranium by ferrous ion reduction in H₃PO₄; solution contains uranium(VI), iron(III), molybdenum(VI), chromium(III), vanadium(IV), HNO₃, and H₂SO₄.

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DETERMINATION OF URANIUM AFTER REDUCTION WITH FERROUS ION IN PHOSPHORIC ACID; TITRATION WITH VANADATE

C. E. Hedrick

Recent studies at the New Brunswick Laboratory (NBL) on the titrimetric method of determining uranium involving the reduction to uranium(IV) by iron(II) in phosphoric acid, selective oxidation of excess iron(II) by nitric acid and molybdate catalyst, and titration with standard dichromate, have shown that the addition of vanadyl ion to the solution being titrated dramatically sharpens the titration endpoint.¹ In the present work, studies were made of the use of sodium vanadate to titrate the reduced uranium without adding vanadyl ion.

Experimental

Reagents and Apparatus

The reducing and oxidizing reagents required to prepare the uranium solution for titration have been described.²

Indicator Solution, prepared by dissolving 1 g. of 4,7-dimethyl-1,10-phenanthroline (G. F. Smith Chemical Company, Columbus, Ohio) in 10 ml. of glacial acetic acid, diluting with 250 ml. of water containing 0.41 g. of ferrous sulfate heptahydrate, and after 1 hr. diluting to 500 ml. with water.

Standard Uranium Solution, prepared by dissolving NBL dingot uranium metal (99.972% U) in HNO_3 and diluting to volume and weight.

Standard Vanadate Solution, prepared by dissolving a weighed amount of vanadium pentoxide and an approximately equal weight of sodium hydroxide in at least ten times its weight of water, cooling and diluting to volume and weight. The pentoxide is ignited to 600°C for 1 hr. before use, and is weighed by difference since the material absorbs water from the air at the rate of about 0.01% per min. in open containers. The vanadate solutions are stable with time.

Procedure

Place a weighed quantity of the standard uranium solution to contain 200 to 300 mg. of uranium in a 400-ml. beaker. Add 2 ml. of 10% H_2SO_4 and evaporate on a water bath. Dissolve the residue in 5 ml. of water.

Add in the order given, swirling between additions, 5 ml. of the sulfamic acid solution, 40 ml. of H_3PO_4 and 5 ml. of ferrous sulfate solution. After 1 min., wash down the beaker sides with

10 ml. of the HNO_3 -molybdate solution and swirl. Wait until the dark brown color that is produced in the solution has disappeared, then allow the solution to stand an additional 3 min. Add 100 ml. of the 1M H_2SO_4 and a magnetic stirrer bar, insert the platinum and calomel electrodes and titrate rapidly to a sharp potential break occurring near 590 mv. Alternatively, omit the insertion of the electrodes, add 1.0 ml. of the indicator, and titrate rapidly to a red to light blue color change.

Determine a blank for the indicator titration directly or by analyzing two aliquots of the uranium solution, one analysis being exactly twice the other. In the latter case, calculate the blank by subtracting the volume of titrant used for the larger aliquot from two times the volume of titrant required for the smaller aliquot. (The blank for the potentiometric titration is essentially zero.)

Results and Discussion

Titration with sodium vanadate gave satisfactory sharp endpoints similar to the dichromate-vanadyl ion titrations. Figure 1 shows the potential (vs. the saturated calomel electrode, SCE) plotted against the fraction titrated for both titration procedures. Also indicated in Figure 1 are the potentials involved in the use of both the ferrous-4,7-dimethyl-1,10-phenanthroline and barium diphenylamine sulfonate indicators. The potential break with the dichromate titration appears to be somewhat larger with a slope of potential increase after the endpoint somewhat greater than that with vanadate.

Titration with vanadate are not new. Ammonium, sodium, and potassium vanadate solutions have been used by many workers^{3,4} in the past. In these procedures, however, indicator titrations only were apparently used, and sharp color changes could only be obtained by the addition of oxalate to diphenylbenzidine or N-phenylanthranilic acid indicators, by adding ferric ions to produce ferrous ions that are titrated as in conventional dichromate titrations, or by the use of concentrated H_2SO_4 media in which the potential of the vanadium(V)/vanadium(IV) couple increases. These steps taken to increase the sharpness of the endpoint are not needed here.

The suitability of vanadium pentoxide as a secondary standard was tested by titrating 200 to 300-mg. amounts of uranium with vanadate solutions prepared from known weights of pentoxide, Table 1. Two analytical procedures were used: weight titrations with ferrous-4,7-dimethyl-1,10-phenanthroline indicator and volumetric-potentiometric titrations. The results show that the pentoxide used was apparently 99.86 to 99.94% pure, the latter value perhaps being more accurate. This particular vanadium pentoxide was Fisher analytical reagent ignited to 600°C for 2 hr. before being weighed.

Brief attempts to prepare a purer pentoxide were made. The commercial oxide has about 0.15% water normally present. Heating this material to 110°C for 2 hr. removes a good portion of this water but about 0.05% still remains. Ignition at 600°C removes this last portion. Heating above 650°C fuses the normally granular free-flowing material and subsequent crushing to a powder

FIGURE 1. POTENTIOMETRIC TITRATION OF URANIUM(IV) BY VANADATE AND BY DICHROMATE WITH VANADIUM(IV) PRESENT.

gives a material that dissolves in sodium hydroxide solution to give a cloudy suspension. Imprecise results are invariably obtained whenever this cloudiness is observed. Some evidence has been obtained that a purification procedure consisting of dissolving small amounts of commercial pentoxide in NH_4OH -hydrogen peroxide, filtering the solution, evaporating to a slurry, and treatment of the filtered material with HNO_3 followed by ignition at 600°C for 2 hr. gives a product assaying very near 100.0%. This approach, along with other purification attempts, may be studied further.

TABLE 1

TITRATION OF URANIUM WITH SODIUM VANADATE SOLUTIONS PREPARED FROM IGNITED COMMERCIAL PENTOXIDE REAGENT

<u>No. of Analyses</u>	<u>Titration Method</u>	<u>Pentoxide Purity, Mean %</u>	<u>Coefficient of Variation, %</u>
9	Weighed increments-indicator	99.86	± 0.05
8	Volume increments-potentiometric	99.94	± 0.09

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X-RAY SPECTROGRAPHIC DETERMINATION OF URANIUM IN URANIUM-ZIRCONIUM SOLUTIONS - A PROGRESS REPORT

A. J. Busch and C. G. Goldbeck

The New Brunswick Laboratory (NBL) has in the past studied the determination of uranium in uranium-aluminum and uranium-stainless steel solutions by X-ray spectrography and procedures for these determinations have been described.^{1,2} In the present work, the determination of uranium in uranium-zirconium solutions was investigated.

The strontium internal standard previously used^{1,2} cannot be used in typical zirconium or zircaloy sample solutions containing appreciable concentrations of sulfuric acid and fluoride ion because of precipitation of the strontium. Yttrium behaves similarly. In addition, the sulfuric acid concentration, which is variable in the solutions, seriously affects the intensity of the uranium emission peaks by absorption.³

Bismuth, used by other investigators,⁴ was found to be a satisfactory internal standard. The sulfuric acid effect was minimized by adjusting the concentration to the approximately constant level of 10% by volume. The proposed procedure is apparently satisfactory at the present time for rapidly surveying the levels of uranium in solution samples.

Experimental

Apparatus and Reagents

X-ray Unit, a Norelco X-ray spectrograph with an inverted optic four-sample chamber, a tungsten target tube operated at 45 kv. and 25 ma. in an air path together with a lithium fluoride analyzing crystal and a scintillation counter with thallium-activated sodium iodide crystal operated at 0.85 kv. A NIM panel is used with a linear amplifier gain of 256 and a single-channel pulse-height analyzer set at a base line of 2.50 v. with a window width of 4.50 v.

Sample Cell, Spex Industries expendable polypropylene with about 8-ml. capacity and 1/4 mil. mylar film held in place with a synthetic rubber "O" ring.

Bismuth Solution, 25.0 mg./ml., prepared by dissolving 6.9675 g. of bismuth trioxide in (1+9) HNO₃ and diluting to 250 ml.

Zirconium Solution, 54.6 mg./ml., prepared by dissolving 21.3 g. of Zr(SO₄)₂·4H₂O in (1+9) H₂SO₄ and diluting to 100 ml.

Uranium Solution, 12.5 mg./ml., in (1+30) H₂SO₄.

Procedure

Standard Curve. Weigh into 25-ml. volumetric flasks 0.5 to 5 ml. aliquots of the uranium solution. Add to each flask 5.00 ml. of the zirconium solution and 1.00 ml. of the bismuth internal standard solution. Dilute the solutions to volume with (1+9) H_2SO_4 . Pour about 7 ml. into the cell.

Measure the uranium $\text{L}\alpha$ peak at $26.14^\circ(2\theta)$ and its background at $30.00^\circ(2\theta)$; the bismuth $\text{L}\alpha$ at $33.02^\circ(2\theta)$, its background at $34.80^\circ(2\theta)$. Calculate the intensity ratios, R_G and R_N , for both gross counts (no background correction) and net counts (background correction), respectively, and plot both R_G and R_N vs. uranium concentration.

Analysis of Samples. Weigh an aliquot of not more than 10 ml. containing less than 60 mg. of uranium into a 25-ml. volumetric flask, add 1.00 ml. of the internal standard solution, and dilute to volume with (1+9) H_2SO_4 . Pour about 7 ml. into the cell and measure as described above for the standard curve preparation.

Results and Discussion

Four synthetically prepared uranium-zircaloy solutions were analyzed by taking both gross and net counts and referring the data to the appropriate standard curve. The two procedures were compared in the hope that the simpler and quicker technique involving no background correction would be satisfactory. From the data in Table 1 it would appear that this technique did tend to give the more accurate results. However, further work would have to be carried out on additional more complex samples to prove that the background counts could always be ignored.

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TABLE 1
ANALYSES OF SYNTHETIC URANIUM-ZIRCONIUM^a SOLUTIONS

Sample No.	Volume Taken, ml.	Uranium, mg./g.		
		Present	Found (Gross Counts)	Found (Net Counts)
1	4	1.10	1.10	1.11
	3		0.93	0.97
	5		1.10	1.10
2	5	5.21	5.20	5.04
	4		5.21	5.13
	9		5.26	5.04
	7		5.13	5.03
3	5	9.00	9.18	9.26
	7		8.98	9.09
	7		8.97	8.92
	8.5		9.04	9.06
4	4	4.55	4.59	4.64
	5		4.56	4.56

a. In addition to the indicated uranium concentration solutions contained about 6.5% zirconium, 8% aluminum nitrate nonahydrate, about 5% HNO₃ and small amounts of HF.

AUTOMATIC DETERMINATION OF URANIUM WITH THE TECHNICON AUTOANALYZER - A PROGRESS REPORT

C. G. Goldbeck

The Technicon Autoanalyzer is basically a multichannel peristaltic pump which feeds the sample and reagents in fixed proportions and in proper sequence into mixing chambers, extractors and phase separators in a continuous stream. The colored solution resulting from mixing the sample with a chromogenic reagent passes through a colorimeter and the transmission is recorded. Sampling is carried out either from a sample device holding sample cups, or with a programmer which opens a specific feed line into the sample stream.

It was desired to determine the possibility of using such an automated system for monitoring uranium in process waste streams. Specifically, the method should be able to determine uranium at the 1 $\mu\text{g./ml.}$ level in an aqueous stream that might contain many other ions. In solutions of this type, it is clear that a separation technique such as extraction would be required in the procedure to separate the uranium from interferences and to concentrate it sufficiently to attain the desired sensitivity with known colorimetric reagents.

Preliminary Studies. French workers¹ have described an automated system with the Technicon Autoanalyzer to monitor the water courses around one of their uranium plants (Pierrelatte). The method involves an extraction with carbon tetrachloride of the uranium-dibenzoylmethane complex in a pyridine medium. A similar system was assembled in the NBL Autoanalyzer with some differences in the flow rates:

<u>Reagent</u>	<u>Flow Rate, ml./min.</u>
(Sample)	2.0
Magnesium nitrate	0.6
Air	1.2
Dibenzoylmethane	2.12
Debubbler	2.0
Cell debubbler	0.16
Carbon tetrachloride	1.06
Cell pump-out	0.7

While the general procedure and sensitivity appeared to be promising, one disadvantage of the system was so serious that it was abandoned before any further work was done on solutions of varying composition. The toxicity and disagreeable odor of the pyridine was considered too intolerable to permit installation in any processing plant.

TBP-Arsenazo III System. A procedure² involving the use of Arsenazo III used in conjunction with a tributyl phosphate (TBP) extraction was then considered. These reagents have both been used separately in the past at NBL, and it was felt that adequate sensitivity could be achieved if the procedure could be adapted to the Autoanalyzer. One difficulty associated with the use of TBP is the tendency to soften or dissolve plastic or rubber tubing such as is used in the pumping and transmission lines of the Autoanalyzer. A water bottle displacement technique, therefore, must be used to inject the solvent into the aqueous sample. However, this organic layer had to be stripped later by passage through a second extraction column, and no direct pumping action could be used to push it through the stripper.

To overcome this difficulty, the flow rates were so adjusted in the extractor column that the TBP layer was pushed into the stripper and mixed with the Arsenazo III reagent. The TBP layer leaving the stripping column was allowed to overflow from the last phase separator without pumping while the aqueous layer was being drawn through the colorimeter. With this arrangement, the extraction and stripping columns worked well enough to demonstrate that adequate sensitivity could be reached. However, the system was not too steady, apparently because the TBP flow was not positive. The excess TBP that went into the first debubbler pump tubing quickly deteriorated that tubing with the result that the flow rate of the TBP being pushed through the stripper was not as constant as it had to be to give consistent results.

To overcome this weakness, a new approach was used: a negative displacement bottle was placed at the outlet of the phase separator which followed the stripping column. Water was pumped out of this bottle and TBP was drawn through the stripping column into the bottle where it was then out of circulation. This system, shown in Figure 1, gave consistent readings with uranium solutions of varying concentrations.

Results and Discussion

With the arrangement shown in Figure 1, the following response is attained:

<u>Uranium Concentration,</u> <u>μg./ml. (3N HNO₃)</u>	<u>Transmission, %</u>
0	100
0.1	95
0.5	77
1.0	60

FIGURE 1. FLOW SHEET OF TBP-ARSENZO III SYSTEM.

The sensitivity is apparently adequate and the standard curve is linear.

Runs made with 1, 2, 3, and 4N acidities showed marked differences presumably because the buffer could not control the final pH well enough. The blank or base line also varied with the acidity of the sample.

The effect of impurity iron and sulfate was tested briefly. Up to 0.1M iron and 0.1M sulfate in the 3N HNO₃ uranium feed solution can be tolerated; higher concentrations interfere by decreasing the color.

Thus, with fairly uniform samples, the present system should be applicable with little difficulty. However, with samples varying greatly in acidity and concentration of interfering impurities, a different system must be found. A more sensitive chromogenic reagent would go far in solving this problem of variable samples because a more dilute final solution could be used.

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ESTIMATION OF GAMMA-RAY SELF ABSORPTION COEFFICIENT IN THE DETERMINATION OF URANIUM-235 IN SOLID SAMPLES

L. C. Nelson, Jr.

A rapid, efficient counting method for the determination of uranium-235 in a wide variety of crushed, solid samples was needed. Counting methods for the analysis of samples more homogeneous and with more constant densities and uranium-235 contents have been used in the past.^{1,2} With these samples the self absorption factors are estimated rather simply by transmission techniques; however, with solid samples of relatively low activity such as calcined ash which vary considerably in density and uranium-235, the type of sample to be analyzed here, these techniques are not practical.

An attempt was made, therefore, to utilize a method for determining the self absorption coefficient developed for the analysis of radium.³ In this method, the self absorption equation:

$$A/A_0 = e^{-\mu x} \quad (1)$$

where A is the measured activity,

A₀ is the unattenuated activity,

μ is the self absorption coefficient,

and x is the mass of the sample in grams,

is changed to the logarithmic form and rearranged to give the straight-line equation:

$$\log A = -\mu x + \log A_0. \quad (2)$$

Thus, the value of μ can be calculated as the slope of the best straight line obtained on measuring the activity of at least 3 samples differing in weight. The least square procedure of determining the best straight line is rather laborious; accordingly, a short computer program was written for this purpose. This technique makes the procedure suitable for routine use.

Equipment

Scintillation Counter. Any suitable well-type, NaI scintillation detector and counter-timer can be used. In this procedure a 4 x 4 inch detector with a 5/8 x 2 3/4 inch well was used.

Sample Vials, 1/2 x 3 inch, of lucite plastic, with a polyethylene snap cap made by Celluplastics, Inc.

Procedure

Sample Preparation and Counting. Fill a tared vial with the ground and mixed sample and tap several times to ensure a uniform density. Weigh the vial and then cap. Prepare 3 or 4 vials of each sample. Count each vial for 10 min.

Calculate the net counts per minute per gram for each vial and convert the counts to the $\log_{10}$ form. By means of the short computer program shown in Appendix I, determine by a least square analysis the slope of the straight line equation, μ , the absorption coefficient. Use the coefficient so determined to correct the sample count rates which are compared to standards similarly corrected. Alternatively, combine this value for the absorption coefficient with other values determined similarly from other similar samples to obtain an average value for a given sample type.

Results

The data obtained on several samples are shown in Table 1. The absorption coefficient, μ , calculated for each sample was used to correct each vial count rate and the corrected value was compared to a standard count rate to obtain the U-235 g./g. shown in the last column. The results of the least square analyses as printed out on the computer teleprinter is shown in Figure 1. Figure 2 shows a plot of sample weight vs. corrected $\log_{10}$ count rate.

The absorption coefficients shown in Table 1 apparently differ significantly. Whether the differences are due to actual sample composition differences or to statistical variations in the measurements has not as yet been determined.

A comparison of the total uranium values obtained by the proposed method and those obtained by a dichromate titration method is shown in Table 2. The chemical method involves the use of much smaller samples, about 1 gram quantities, and accordingly, the effect of sample segregation must be considered here since these samples are known to be generally heterogeneous. The total uranium values for the proposed method were calculated from the uranium-235 values given in Table 1 together with the known isotopic abundance values as determined mass spectrometrically.

TABLE 1

EXPERIMENTAL DATA USED TO CALCULATE ABSORPTION COEFFICIENT

Sample Weight g.	Net C/M	C/M/g. Uncorrected	Log ₁₀ C/M/g.	Absorption Coefficient, μ	C/M/g. Corrected	U-235 g./g.	g./g. U
7.393	304,866	41,238	4.615		44,366	0.01469	0.01578
6.981	301,352	43,176	4.635	-0.0099	46,227	0.01530	0.01643
5.400	235,614	43,632	4.640		46,030	0.01524	0.01637
6.233	547,358	87,816	4.944		95,060	0.03148	0.03381
6.597	568,144	86,121	4.935	-0.0131	93,885	0.03109	0.03339
6.527	559,917	85,784	4.933		93,447	0.03094	0.03323
5.636	494,048	87,659	4.943		94,369	0.03125	0.03356
7.062	404,186	57,248	4.758		60,344	0.01998	0.02146
7.570	434,856	57,444	4.759	-0.0076	60,845	0.02015	0.02164
6.499	379,709	58,426	4.767		61,385	0.02033	0.02183
14.180	480,988	34,530	4.538		39,172	0.01297	0.01329
13.898	473,583	34,080	4.532	-0.0089	38,561	0.01277	0.01309
15.086	504,500	33,450	4.524		38,250	0.01266	0.01298
14.842	472,488	31,830	4.503		35,841	0.01187	0.01217
14.117	454,043	32,250	4.508	-0.0080	36,102	0.01195	0.01225
15,611	489,439	31,330	4.496		35,497	0.01175	0.01204
13.622	433,901	31,860	4.504		38,409	0.01271	0.01303
14.622	453,060	31,000	4.491	-0.0137	37,865	0.01254	0.01285
14.985	457,967	30,570	4.485		37,532	0.01243	0.01274

*GO
NUMBER OF POINTS :3

X	Y	XY	X SQ
:7.393	:4.615	=+ 34.1187	=+ 54.6565
: 6.981	:4.635	=+ 32.3569	=+ 48.7344
: 5.400	:4.640	=+ 25.0560	=+ 29.1600
=+ 19.7740	=+ 13.8900	=+ 91.5316	=+ 132.5510
S LOPE =- 0.0099			
INTERCEPT =+ 4.6955			
*			

FIGURE 1. TYPICAL LEAST SQUARE ANALYSIS

FIGURE 2. LOG OF SAMPLE COUNT RATE VERSUS SAMPLE WEIGHT

TABLE 2

COMPARISON OF RESULTS - PROPOSED METHOD AND TITRATION METHOD

<u>Sample No. 1</u>	<u>Total Uranium g./g.</u>	
	<u>Counting Method^a</u>	<u>Titration Method</u>
1	0.0158, 0.0164, 0.0164	0.0163
2	0.0338, 0.0334, 0.0332, 0.0336	0.0351
3	0.0215, 0.0216, 0.0218	0.0208
4	0.0133, 0.0131, 0.0130	0.0136
5	0.0122, 0.0123, 0.0120	0.0131
6	0.0130, 0.0129, 0.0127	0.0130

a. Calculated from the U-235 values and the isotopic ratio values obtained mass spectrometrically.

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C-FOCAL., 1968

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01.01 C-LEAST SQUARE FIT TO A STRAIGHT LINE EQUATION Y=MX+B
01.05 E
01.10 A "NUMBER OF POINTS ",N, !!
01.20 T "      X      Y      XY      X SQ",!!
01.30 A "      ",X,"      ",Y,"      "; DO 2.0
01.40 I (C-N)1.30,3.10

02.10 S SX=SX+X; S SY=SY+Y
02.20 S Z=X*Y; S Y=X*X
02.30 T Z,"      ",Y,!
02.40 S XY=XY+Z; S X2=X2+Y
02.50 S C=C+1

03.10 S M=[XY-(SX*SY)/N]/[X2-(SX)2/N]
03.20 S B=[(SX)*(XY)-(SY)*(X2)]/[X2-N*(X2)]
03.25 T !,SX,"      ",SY,"      ",XY,"      ",X2, !!
03.30 T "SLOPE ",M,!,"INTERCEPT ",B,!!
03.40 Q
*
```

*GO
NUMBER OF POINTS :5

X	Y	XY	X SQ
:5.000	:1.000	=+ 5.0000	=+ 25.0000
: 6.000	:2.000	=+ 12.0000	=+ 36.0000
:7.000	:3.000	=+ 21.0000	=+ 49.0000
:8.000	:4.000	=+ 32.0000	=+ 64.0000
:9.000	:5.000	=+ 45.0000	=+ 81.0000
=+ 35.0000	=+ 15.0000	=+ 115.0000	=+ 255.0000
S LOPE =+ 1.0000			
I NTERCEPT =- 4.0000			

*

APPENDIX I - FOCAL PROGRAM FOR LEAST SQUARE ANALYSIS

CONTROLLED POTENTIAL COULOMETRIC DETERMINATION OF PLUTONIUM

K. Lewis

Problems encountered in the utilization of the controlled potential coulometric determination of plutonium in this laboratory were summarized in a previous report.¹ Further work with this technique since that time has led to more reliable results which are apparently associated with a consistent treatment of the solutions before titration.

Experimental

Apparatus

Coulometer. Solid-state version of the ORNL Model Q-2564 controlled-potential coulometric titrator.²

Cell. Fifty-ml. lipless beakers with fitted teflon cap and rubber O-ring.

Standard Solutions

1. Plutonium metal (NBS 949B) is dissolved in 6N HCl, then evaporated two times with (1+1) HNO₃. The residue is diluted to the desired concentration with 8N HNO₃.

2. Plutonium sulfate (NBS 944) is dissolved directly in 8N HNO₃ to the desired concentration.

Procedure

Sample Preparation. Transfer a solution containing from 1 to 3 mg. of plutonium directly to the coulometric cell by washing with 0.5M H₂SO₄. After adding 3 to 5 drops of H₂SO₄, evaporate the solution to dryness under an infrared lamp. Dissolve the residue with a minimum of 0.5M H₂SO₄, add 5 drops of H₂SO₄ and evaporate to dryness two times. Finally, dissolve the residue in 1.0M HClO₄-0.02M sulfamic acid for the analysis.

Chemical Calibration. Prepare known amounts of plutonium as above. Carry out a reduction titration at +0.56 v. vs. the SCE until the current decreases to 30 μ a. At this point, titrate by oxidation at +0.88 v. until the current falls to 30 μ a. Record the final integrated voltage and calculate the chemical calibration value by dividing the weight of sample in milligrams by the voltage readout of the oxidation step.

Sample Analysis. Prepare solutions and titrate as described above. Determine the milligrams of plutonium in the sample by multiplying the final voltage readout by the chemical calibration factor.

Results and Discussion

In this study, chemical calibration (instead of electrical calibration) was used exclusively. The results obtained for the chemical calibration illustrate the precision attained by the method. Seven standard solutions prepared from both plutonium sulfate and plutonium metal were coulometrically titrated to determine the chemical calibration factor. The coefficient of variation of the average value was 0.05%. A further check on the reliability of the titration was determined by analyzing another known plutonium solution prepared from plutonium sulfate. Nine aliquots of this solution were titrated and the plutonium content was calculated with the results shown in Table 1.

TABLE 1

ACCURACY AND PRECISION OF PLUTONIUM DETERMINATION

<u>Sample</u>	<u>No. of Determi- nations</u>	<u>Plutonium, mg./ml.</u>		<u>Error, %</u>	<u>Coefficient of Variation, %</u>
		<u>Taken</u>	<u>Found</u>		
PuS-12	9	0.9604	0.9600	-0.04	0.03

Two different platinum electrodes were used during the course of the work. The calibration values of the two electrodes differed by as much as 0.5%; one electrode maintained a constant value over the time period it was used whereas the other changed periodically. It is thus necessary to titrate a standard solution at intervals to check on the chemical calibration value. It was also noted in the course of titrating different samples that the precision of the titration is apparently adversely affected by certain solutions. The possible reasons for this behavior have not yet been investigated.

A comparison of the present results with the problems previously observed on platinum electrodes indicates that the improvement in the reliability of the titration is associated with the treatment of the solution before titration. Work is continuing on the controlled potential coulometric titration of plutonium to determine the types of solutions that can be analyzed, the reasons for the effectiveness of the solution treatment and which solution components lead to poorer precision.

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A TEN-YEAR EVALUATION OF THE STABILITY OF PLUTONIUM SULFATE TETRAHYDRATE

C. E. Pietri and A. W. Wenzel

It had been suspected that plutonium sulfate tetrahydrate, a proposed primary standard for plutonium, might be susceptible to decomposition because of the effect of alpha-radiolysis on the water of crystallization. An initial study¹ of the stability involving periodic analyses^{2,3} indicated that the material, stored in screw-capped glass bottles in a gloved box with a nominal 40% relative humidity, was stable for at least 28 months. The present investigation continues this study. The stability of several lots of the material was determined under the same conditions for 32-, 63-, 75-, and 120-month periods. In addition, the stability under extremes of relative humidity was studied.

All the long term data indicate that plutonium sulfate tetrahydrate is stable for periods of up to 10 years under the conditions existing in a conventional gloved box. Relative humidity extremes have only temporary effects on the stoichiometry. A more detailed report is being prepared for publication at a later date.

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THE EFFECT OF EXPOSURE OF PLUTONIUM SULFATE TETRAHYDRATE TO ENVIRONMENTS WITH EXTREME HUMIDITIES

C. E. Pietri and R. I. Greenberg

A previous study of the stability of plutonium sulfate tetrahydrate, $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, a proposed primary standard for plutonium, indicated that the material was unaffected by changes in relative humidity (R.H.) from 17 to 75%.¹ The present investigation was made to determine the effect on the compound of exposure to high humidity (95% R.H.) followed by drying at 40% R.H. and at <0.1% R.H., and of exposure to low humidity, <0.1% R.H., after storage in the stable 17 to 75% R.H. range.

In all tests, the samples were initially assayed for plutonium and weighed, then placed into the test humidities, weighed periodically, and reassayed after exposure to the original environment in order to detect possible changes in stoichiometry arising from the test conditions. Two series of tests were run concurrently, each using three samples of $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ prepared for the National Bureau of Standards for use as standard material. In the first series, the samples were exposed to 95% R.H. for 22 days; the average weight gain, which confirmed previous findings, was 0.2%. The samples were then placed in 40% R.H. for 5 days, and assayed for plutonium content. The analyses showed that the samples lost the added weight and now did not differ significantly from the original weight and plutonium assay. Again, the samples were exposed to 95% R.H. for 19 days and a weight gain was noted as before. They were then placed in an environment of <0.1% R.H. (desiccation with P_2O_5) for 27 days. This treatment gave a final average weight loss of 0.06%. On subsequent exposure to 40% R.H. for 5 days, the samples regained the lost weight and the plutonium content did not differ significantly from the original value.

The three other samples were taken directly from 40% R.H. without any previous exposure to environments outside of the 17 to 75% R.H. stability range and placed in <0.1% R.H. for 45 days. The average weight loss was about 0.07%. On exposure to 40% R.H., the weight loss was regained and the plutonium assay did not differ from its initial value.

In both series of tests the original weight of the material was obtained, after testing at <0.1% and 95% R.H., by overnight (16 hours) exposure to 40% R.H.

The results of this investigation indicate that although plutonium sulfate tetrahydrate gains weight upon exposure to high humidity it can be readily dried to its original weight without change in its plutonium content. The material can be used in "dry boxes" of extremely low humidity (as may be required in some operations) if an accuracy greater than 0.1% is not necessary.

Any loss in weight at very low humidity can be readily regained without affecting the plutonium content of the compound. Thus, exposure of the tetrahydrate to extremes of humidity does not affect the plutonium content of the compound after re-equilibration at 40% R.H. However, the effect of long-term exposure of plutonium sulfate tetrahydrate at very low or very high humidities was not investigated and present results should not be extrapolated for extended periods of time.

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DETERMINATION OF PLUTONIUM BY ISOTOPE DILUTION MASS SPECTROMETRY.
I. EFFECT OF VARIATION OF TRACER TO SAMPLE RATIO

D. Dees, A. W. Wenzel, H. N. Simmons, H. O. Finley,
and C. E. Pietri

Isotope dilution mass spectrometry has been used at this laboratory for the determination of U and Pu in dissolver-type solutions for several years.¹ The tracers used, Pu²⁴² and U²³³, have been added in about a 1:1 ratio to the Pu and U isotopes of interest in the sample, usually Pu²³⁹ and U²³⁵ or U²³⁸. Since the estimates of the U and Pu content of dissolver solutions may vary considerably, the tracer to sample ratio may differ from 1:1. Accordingly, a program was initiated to determine the reliability of measurements taken outside of the nominal 1:1 ratio range, specifically, for ratios of tracer to sample of 1:2 and 2:1.

The preparation and calibration of tracer solutions, standards, and samples, and the mass spectrometric procedures employed in this investigation have been given previously.¹ The Pu²⁴² tracer used had the following isotopic composition in wt. %: Pu²³⁸, 0.004; Pu²³⁹, 0.018; Pu²⁴⁰, 0.033; Pu²⁴¹, 99.891; and was calibrated against NBS No. 944 Pu(SO₄)₂·4H₂O with the following composition in wt. %: Pu²³⁹, 97.694; Pu²⁴⁰, 2.236, Pu²⁴¹, 0.0687; Pu²⁴², 0.0014. The synthetic solution used for the standard samples was prepared to contain 7.696 μ g. Pu/sample; it also contained about 1.8 mg. U/sample in order to simulate a dissolver solution. Four samples of this synthetic solution were spiked with Pu²⁴² tracer in the sample to tracer ratio of 1:2 and four in the ratio of 2:1. The results of this study are shown in Tables 1 and 2.

TABLE 1

DETERMINATION OF PLUTONIUM BY ISOTOPE DILUTION MASS
SPECTROMETRY: Pu²⁴² TRACER TO SAMPLE RATIO 2:1

<u>Pu Added, μg.</u>	<u>Pu Found, μg.</u>	<u>Relative Difference, %</u>
7.696	7.709	+ 0.17
7.696	7.706	+ 0.13
7.696	7.702	+ 0.08
7.696	7.710	+ 0.18

Average Relative Difference $\pm$ 95% C.L. = + 0.14 $\pm$ 0.55

TABLE 2

DETERMINATION OF PLUTONIUM BY ISOTOPE DILUTION MASS
SPECTROMETRY: Pu²⁴² TRACER TO SAMPLE RATIO 1:2

<u>Pu Added, $\mu\text{g.}$</u>	<u>Pu Found, $\mu\text{g.}$</u>	<u>Relative Difference, %</u>
7.696	7.699	+ 0.04
7.696	7.695	- 0.01
7.696	7.684	- 0.16
7.696	7.692	+ 0.05

Average Relative Difference $\pm 95\%$ C. L. = -0.04 ± 0.33

The average relative differences given in Tables 1 and 2 do not differ significantly from that obtained with 1:1 ratios: $+ 0.12 \pm 0.17\%$. Therefore, estimates of the plutonium content of dissolver-type solutions could vary 100% without affecting the isotope dilution results.

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THE DETERMINATION OF URANIUM IN URANIUM-PLUTONIUM MIXTURES
BY FERROUS REDUCTION IN PHOSPHORIC ACID AND POTASSIUM
DICHROMATE TITRATION: AN EVALUATION

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

The determination of uranium without prior separation of iron, chromium, nitrate, and other ions which interfere in conventional titrimetric methods has been described by Davies and Gray.¹ The method was evaluated at the New Brunswick Laboratory (NBL) by Eberle and Lerner.² The method consists of the following steps: uranium(VI) in concentrated phosphoric acid containing sulfamic acid is reduced by ferrous sulfate; the excess ferrous ion is oxidized by nitric acid in the presence of molybdenum(VI) catalyst; dilute sulfuric acid is added, and the uranium(IV) is titrated with standard potassium dichromate to either an indicator or potentiometric endpoint.

Davies and Gray reported that uranium could be determined in the presence of plutonium, and limited data obtained at NBL confirmed that plutonium did not interfere. In the present study, a further evaluation was made by analyzing uranium-plutonium synthetic solutions to simulate uranium dioxide-plutonium dioxide samples with a 20% plutonium content. The analyses were made by a greatly improved method³ involving the addition of vanadyl ion to the diluent. This modification dramatically sharpens the endpoint, previously found to be somewhat sluggish and requiring some experience to locate. In addition an improvement was subsequently made in the reagent addition to avoid the precipitation of plutonium. The effect of americium as a possible interference was also studied because Am^{241} is commonly found with plutonium as a result of its formation from radioactive decay of Pu^{241} . A comparison of indicator versus potentiometric endpoint detection was also made.

Experimental

Reagents

Sulfamic Acid, 1.5M. Dissolve 75 g. in 500 ml. of H_2O .

Ferrous Sulfate, 1.0M. Add 25 ml. of H_2SO_4 cautiously to 25 ml. of H_2O , cool the solution, add 75 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, dilute to 250 ml. with H_2O and shake to dissolve. Prepare fresh weekly.

Nitric Acid, 8M - Sulfamic Acid, 0.15M - Ammonium Molybdate, 0.4%. Dissolve 4.0 g. of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 400 ml. of H_2O . Add 500 ml. of colorless HNO_3 , mix, add 100 ml. of 1.5M sulfamic acid and mix. Prepare fresh every three weeks.

Sulfuric Acid, 2N. Use sulfuric found to be low in reducible materials. (Merck reagent-grade acid is satisfactory.)

Vanadyl Sulfate, 0.05M. Dissolve 4.9 g. of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ in 500 ml. of H_2O .

Potassium Dichromate Standard Solution, 3.5 mg. $\text{K}_2\text{Cr}_2\text{O}_7/\text{g.}$
Solution. Dissolve 7.3000 g. of primary standard $\text{K}_2\text{Cr}_2\text{O}_7$ (previously dried at 120°C for 1 hr.) in 1N H_2SO_4 in a weighed 2 liter volumetric flask. Dilute to 2 liters with 1N H_2SO_4 and reweigh. Correct all weights for buoyancy effects. Standardize the solution against NBL uranium dingot uranium (99.972% U) by the method below to confirm the titer.

Barium Diphenylamine Sulfonate Indicator, 0.04%. Dissolve 0.2 g. of reagent in about 400 ml. of near-boiling H_2O . Cool and dilute to 500 ml.

Plutonium-Uranium Synthetic Solutions. Prepare individual samples of a uranium-plutonium mixture by dissolving weighed portions of $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (NBS No. 944) and U_3O_8 (NBS No. 950a) in 8N HNO_3 . (The nominal U:Pu weight ratio was about 4:1; the uranium content varied from about 135 to 275 mg. per sample. For studying the effect of americium on the uranium determination, a $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ prepared at this laboratory was used in place of the NBS certified material.)

Apparatus

pH Meter, with millivolt scale, equipped with platinum and calomel electrodes.

Procedure.

1. Weigh a uranium-plutonium sample containing ideally 200 to 300 mg. of uranium into a 250-ml. teflon beaker. Dissolve the sample with about 25 ml. of 8N HNO_3 (plus 3 drops of HF, if necessary). If the HNO_3 -HF treatment is not satisfactory, fuse the sample with 10 g. of NaHSO_4 and dissolve the melt according to a reported procedure.⁴

2. Transfer the sample quantitatively to a 400-ml. beaker, add 10 ml. of 1N H_2SO_4 , and evaporate to moistness without fuming.

3. Add a magnetic stirring bar to the beaker and dissolve the residue in 15 ml. of H_2O being sure to wash down the sides of the beaker.

4. Add 5 ml. of 1.5M sulfamic acid and swirl to mix thoroughly.

5. Add 20 ml. of H_3PO_4 and mix thoroughly. (In the presence of plutonium, a precipitate forms and then partially dissolves.)

6. Add 10 ml. of H_2O and mix thoroughly until the precipitate dissolves.

7. Add 40 ml. of H_3PO_4 , washing down the sides of the beaker with the H_3PO_4 .

8. For 200 mg. of uranium, add about 5 ml. of ferrous sulfate solution. For 300 mg. of uranium, add about 7 ml. of

ferrous sulfate solution. Add the ferrous sulfate solution directly to the uranium solution being careful not to splash or wet the walls of the beaker with the solution. Swirl thoroughly and wait 5 min.

9. Add 10 ml. of the HNO_3 -ammonium molybdate solution, rinsing down the sides of the beaker. Swirl to mix, and then wait 3 min. after the disappearance of the dark color. (The solution must be thoroughly mixed so that all the ferrous solution is contacted.)

10. Add 100 ml. of 2N H_2SO_4 to 10 ml. of vanadyl sulfate solution in a graduate, add this combined solution to the sample solution and mix thoroughly using the magnetic stirrer. Avoid aerating the solution by not allowing the stirrer to agitate violently.

11. Quickly insert the electrodes into the solution.

12. From a preweighed weight buret filled with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution, immediately titrate rapidly to a potentiometric endpoint which begins at about 520 and occurs about 600 mv. (The magnitude of the break is about 130 to 150 mv.) Reweigh the buret. Complete the titration within 3 min. after dilution of the solution in step 10.

13. If an indicator endpoint is used, add 2 ml. of the indicator solution to the composite in step 10 and eliminate the electrodes in step 11. Rapidly titrate the green solution to a purple endpoint. Correct the sample titration for the indicator blank by titrating two aliquots of the same solution, one aliquot being exactly one-half of the other. (The blank is equal to twice the volume of titrant required for the less concentrated solution minus the volume required for the more concentrated and usually amounts to about 0.08 grams of potassium dichromate solution.)

Results and Discussion

Titration Technique. Weight titrations were used in all studies. Titration by weight rather than volume is preferred for gloved-box work at this laboratory since the former technique is not affected by temperature changes and provides for easier manipulation in addition to affording greater accuracy.

Turbidity During Titration and Reproducibility. Preliminary work with uranium-plutonium solutions was done by titration to the barium diphenylamine sulfonate indicator endpoint. In this procedure the initial sample volume was limited to the required 15 ml. maximum but varied, in fact, as low as 5 ml. In the presence of plutonium, turbidity sometimes resulted on addition of the H_3PO_4 and sporadic results low by 0.3 to 0.4% occurred. A modification of the procedure in which the initial sample volume was maintained at 15 ml. by dilution with water when necessary followed by successive addition of sulfamic acid, phosphoric acid, water, and further addition of phosphoric acid gave clear solutions and reproducible titration data. This modification increased the total volume of solution by 10 ml. of water and 20 ml. of phosphoric acid. Results from two series of tests using about 135 and 275 mg. of uranium gave a coefficient of variation of 0.06% for each set with no significant bias, Table 1.

TABLE 1

THE DETERMINATION OF URANIUM IN SYNTHETIC URANIUM-PLUTONIUM
SOLUTIONS (INDICATOR ENDPOINT)

Uranium, mg.			
Set No. 1		Set No. 2	
<u>Added</u>	<u>Found</u>	<u>Added</u>	<u>Found</u>
136.78	136.67	275.86	275.91
134.62	134.66	275.66	275.49
135.55	135.47	275.80	275.60
135.86	135.83	275.87	275.67
135.22	135.17	275.69	275.61
135.48	135.36	276.17	276.20
Difference ($\pm$ 95% confidence limits): -0.06 ± 0.09		Difference ($\pm$ 95% confidence limits): -0.09 ± 0.16	
Coefficient of Variation, %: 0.06		Coefficient of Variation, %: 0.06	

Americium Interference. Am^{241} is a common impurity as a result of radioactive in-growth from Pu^{241} decay. The effect of americium on the uranium titration was studied using a uranium-plutonium mixture which had a 0.22% Am^{241} content. The results, Table 2, indicate that the determination was not affected by americium at the concentration studied.

TABLE 2

THE EFFECT OF AMERICIUM ON URANIUM DETERMINATION
(SYNTHETIC U-Pu SOLUTIONS)

Uranium, mg.*	
<u>Added</u>	<u>Found</u>
275.51	275.26
275.65	275.41
272.62	272.43
275.91	275.77
276.11	276.00

Difference ($\pm$ 95% confidence limits): -0.19 ± 0.27

* Am^{241} content = 0.22%

Blank Variation. The indicator blanks, although nominally amounting to about 0.08 grams of dichromate solution, were found to vary by a small amount randomly from day to day. It was suspected that the blank might also vary during any one-day series of determinations. Six blank determinations, made at periodic intervals throughout one day, gave an average value of 0.0864 ± 0.02321 g. $K_2Cr_2O_7$ solution. This variation in the blank, apparently greater than that experienced with other uranium mixtures,² could give rise to a maximum error of 0.09%.

Potentiometric Titration. The variability of the blank correction for indicator titrations prompted the evaluation of the potentiometric endpoint detection for the uranium determination in uranium-plutonium solutions. The data in Table 3 for synthetic uranium-plutonium solutions show a coefficient of variation of 0.03% with no significant bias. This smaller variability for the potentiometric endpoint method than for the indicator endpoint is undoubtedly due to the error contributed by the blank correction. Uranium was determined also in actual samples of UO_2 - PuO_2 utilizing both the indicator and the potentiometric endpoint detection for comparison purposes, Table 4.

TABLE 3

THE DETERMINATION OF URANIUM IN SYNTHETIC URANIUM-PLUTONIUM SOLUTIONS (POTENTIOMETRIC ENDPOINT)

Uranium, mg.	
<u>Added</u>	<u>Found</u>
260.86	260.79
259.98	260.07
216.28	216.20
240.48	240.41
252.78	252.67
208.93	208.92
241.45	241.47
241.45	241.42

Difference ($\pm$ 95% confidence limits): -0.03 ± 0.06

Coefficient of Variation, %: 0.03

TABLE 4

COMPARATIVE ANALYSES OF PuO_2 - UO_2 SAMPLES

Sample No.	Uranium, %	
	Potentiometric Endpoint	Indicator Endpoint
1	70.44	70.44
	70.40	70.48
	70.39	70.42
	70.47	70.39
	70.42	
	70.39	
	70.41	
	<u>70.44</u>	
	Average: 70.42	Average: 70.43
	Coefficient of Variation, % : 0.04	Coefficient of Variation, % : 0.06
2	60.27	60.28
	<u>60.27</u>	<u>60.30</u>
	Average: 60.27	Average: 60.29

There are indications in Tables 1 and 3 that the titration may give slightly low results although the results statistically do not differ significantly at the 95% confidence level. This phenomenon may be caused by some slight air oxidation of uranium-(IV) after the sulfuric acid dilution step and prior to the completion of the titration.³ Therefore, it is important that this period be kept to 3 min. or less to hold the error within this acceptable level.

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2. Eberle, A. R. and Lerner, M. W., NBL-247 (April 1969), p. 1.
3. Eberle, A. R. and Lerner, M. W., NBL Unpublished Information, 1969.
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DETERMINATION OF CARBON IN BORON AND BORON CARBIDE

T. D. Tarr and C. G. Goldbeck

A method for the determination of carbon in boron involving burning the sample in oxygen and a lead peroxide flux, collecting the carbon dioxide formed in a barium hydroxide solution and titrating the excess barium hydroxide with hydrochloric acid has been used at the New Brunswick Laboratory (NBL) in the past.¹ This procedure, while simple and rugged, has been suspected of giving low results on certain elemental and carbide samples.

Another commonly applied method is one in which a high-frequency induction furnace coupled with a gas chromatograph as described by Walker and coworkers^{2,3} is used. In this method, boron is mixed with a combined flux of iron, tin, and copper metal in a Leco crucible. Combustion is achieved by placing the crucible in the high-frequency induction field and passing a jet of oxygen over it. The carbon dioxide is measured by the gas chromatograph. National Bureau of Standards steel samples are used to calibrate the gas chromatograph.

The results of several analyses carried out by both methods are shown in Table 1. It can be seen that the peroxide fusion method gives lower results with both elemental and boron carbide samples, and the carbide results tend to be erratic. As a result of this study, carbon determination in elemental boron and boron carbide are now being carried out routinely with the induction heating-gas chromatography method.

REFERENCES

1. Goldbeck, C. G., New Brunswick Laboratory Procedure, 1961.
2. Kuo, C., Bender, G. T., and Walker, J. M., Anal. Chem., **35**, 1505 (1963).
3. Walker, J. M. and Kuo, C., Anal. Chem., **35**, 2017 (1963).

TABLE 1

COMPARISON OF RESULTS FOR CARBON IN BORON AND BORON CARBIDE

Sample NBL No.	Carbon, %	
	Peroxide Fusion	Induction Heating
F-4359 ^{a, c}	0.736, 0.772, 0.827 0.790	1.30, 1.35, 1.33 1.32, 1.30
F-4360 ^{a, c}	0.600, 0.598	0.880, 0.858, 0.873 0.863, 0.875
F-2929 ^{b, c}	18.3, 20.5, 14.4, 15.1 19.9, 22.6, 17.2, 18.8	---
F-2929 ^{b, d}	21.5, 21.9, 21.7	---
F-2934 ^{b, d}	21.6, 19.7, 19.6, 22.6, 22.3, 13.3, 15.2, 16.5	23.9, 23.7
F-2935 ^{b, d}	22.6, 17.8, 22.3	24.2, 23.6

Notes: a. Boron; b. Boron carbide; c. 1200°C,
d. 1410°C, referring to peroxide fusion
temperature.

PREPARATION OF BORON-FILLED SILICONE ELASTOMER FOR EMISSION SPECTROGRAPHIC ANALYSIS

H. G. Yuster

Spectrochemical analysis of boron-filled silicone elastomer requires the destruction of the organic material, removal of the large quantities of both boron and silicon, and the incorporation of the residue into a suitable matrix for comparison with conveniently made standards. To apply the procedure developed for the treatment of unfilled silicone elastomer prior to analysis,¹ a modification must be made to dissolve the elemental boron.

Experimental

Reagents

H₂SO₄, HF, and HNO₃, redistilled.

Procedure

Cut the sample into 1/4-inch cubes with a razor blade and weigh a 1-g. sample into a 125-ml. platinum dish. Pickle the sample with (1+4) HNO₃ to remove surface contamination and wash with water.

Add 25 ml. of HNO₃ and place the dish on a hot plate at low heat. If the reaction gets too vigorous, remove the dish and cool it in an ice-bath. Digest the covered solution on the hot plate until decomposition is essentially complete.

To remove the silicon and boron, add 15 ml. of H₂SO₄ and 25 ml. of HF. Evaporate to fumes and, if any solid residue still remains, add HNO₃ dropwise (caution) until the solution clears. Cool the dish, add an additional 15 ml. of HF, and again take to fumes. Add once again 10 ml. of HF to the cooled solution and again heat to fumes. Finally, add 20 ml. of water to the cooled solution and evaporate to fumes to ensure the elimination of fluoride. (The final volume of solution should be about 2 ml. at this point.)

Add 100 mg. of gallium as a nitrate solution to the dish and evaporate the contents to dryness under an infra-red lamp. Ignite the residue in a muffle furnace at 900°C for 1 hr. Determine the impurities in the gallium oxide matrix as previously described.²

Discussion

With certain samples of boron elastomer the beryllium content is higher than the standards which range from 1000 to 10,000 p.p.m. In this case, a portion of the gallium oxide matrix is diluted

with gallium oxide in a (1+9) ratio and then compared with the standards. The ratios of Be 3131.07A to Ga 3004.06A are used. Since the original preparation gives a 10X concentration, this 10X dilution gives a beryllium value as determined directly from the standard curve.

To determine any effect of large concentrations of beryllium on the spectral response of the other impurities, the chromium value in this type of sample was studied before and after the dilution required to bring the beryllium down to the optimum level for densitometric measurement. In a group of ten samples analyzed for chromium an average relative difference of 8.5% was found between the concentrated and diluted preparations. This difference is within the precision of the analysis.

REFERENCES

1. Yuster, H. G., NBL-247 (April 1969), p. 46.
2. Yuster, H. G. and Mullin, H. R., NBL-210 (June 1964), p. 21.

ANALYSIS OF SILICONE ELASTOMERS BY ATOMIC ABSORPTION SPECTROSCOPY

R. L. Graff and H. G. Yuster

The determination of impurities in high-purity silicone elastomers by atomic absorption spectroscopy requires the destruction of the organic material and concurrent removal of the large quantity of silica produced which is difficult to keep in solution and which would interfere with efficient burner operation. Moreover, it is desirable to concentrate the low levels of impurities so that the optimum ranges of determination for the instrument are approached as closely as possible. The dissolution procedure¹ developed for the emission spectrographic analysis of silicone elastomers accomplishes both of these objectives and is used here. Comparative results obtained by both atomic absorption and emission spectroscopy are presented.

Experimental

Reagents

H₂SO₄ and HF, redistilled.

Procedure

Cut the elastomer with a razor blade into 1/4-inch cubes and place a 20-gram sample in a 300-ml. platinum dish. Pickle the cubes with a (1+4) HNO₃ solution to remove surface contamination and wash thoroughly with water.

Add 35 ml. of H₂SO₄ and warm on a hot plate at low heat until decomposition occurs. Cool the syrupy, frothing mixture and add slowly 25 ml. of HF. Heat on the plate at moderate heat to complete the decomposition. Cool the dish and add 25 ml. additional HF slowly. Heat the dish to fumes. Repeat the addition of 25 ml. HF and fuming twice more. Wash down the dish with water and heat to fumes twice. Finally, dilute the final volume of about 5 ml. of H₂SO₄ to 200 ml. in a volumetric flask. Compare the sample solution directly with standards prepared in 2.5% H₂SO₄.

(Generally, 100 ml. of sample solution is sufficient. The remaining 100 ml. can be incorporated into a gallium oxide matrix for emission spectroscopic analysis as previously described.² The comparative results given below were obtained by this procedure.)

Results and Discussion

The analyses of samples by both atomic absorption and emission spectroscopy are compared in Table 1. Table 2 presents

TABLE 1

COMPARISON OF ATOMIC ABSORPTION AND EMISSION
SPECTROSCOPIC RESULTS ON ELASTOMER SAMPLES

Element	Impurity, p.p.m. ^a							
	NBL F4713		NBL F4714		NBL F5643		NBL F5644	
	AA	ES	AA	ES	AA	ES	AA	ES
Al	3	2	4	5	7	7	5	5
Ca	1.6	1	3.6	4	4	2	6	3
Cu	0.4	0.29	0.5	0.47	0.7	0.61	0.8	0.32
Cr	0.8	0.46	0.6	0.32	0.4	0.22	0.6	0.44
Fe	4	4	9	9	3.3	3	4	4
Mg	0.6	0.7	2.6	1.5	1.5	1	1.2	1
Ni	2.3	0.31	2.3	0.32	3	0.21	4	0.24
Na	1.5	1	4	3	3.5	5	3.7	5
K	35	30	33	40	38	30	38	30

a. Sample basis.

TABLE 2

COMPARISON OF DUPLICATE PREPARATIONS

Element	Impurity, p.p.m. ^a			
	NBL F4772 (1)		NBL F4772 (2)	
	AA	ES	AA	ES
Al	4	6	5.5	6
Ca	5.2	5.8	5.2	6.6
Cu	0.3	0.50	0.3	0.52
Cr	0.6	0.43	0.6	0.51
Fe	7	12	8	12
Mg	2.6	2.2	2.6	2.2
Ni	1.2	0.20	0.9	0.20
Na	3	3	3.9	3
K	30	30	29	30

a. Sample basis.

atomic absorption data obtained with duplicate preparations of the same sample. In Table 3, the atomic absorption data were obtained by a 10X concentration factor (50 gram sample diluted to 50 ml.). The agreement for all elements except nickel is seen to be satisfactory. The difference in the nickel values is still under investigation.

TABLE 3

COMPARATIVE RESULTS WITH DIFFERENT CONCENTRATION FACTORS

<u>Element</u>	Impurity, p.p.m. ^a			
	<u>NBL F5697-1</u>		<u>NBL F5697-2</u>	
	<u>AA</u> ^b	<u>ES</u>	<u>AA</u> ^b	<u>ES</u>
Al	4	6	4	7
Ca	0.95	0.80	0.85	0.95
Cu	0.13	0.16	0.12	0.16
Cr	0.14	0.17	0.11	0.16
Fe	1.7	2.4	1.3	2.5
Mg	0.4	0.8	0.5	0.9
Ni	0.8	0.13	0.85	0.15
Na	1.7	1	1.7	1
K	40	30	41	30

a. Sample basis.

b. Concentration factor of 10X.

REFERENCES

1. Yuster, H. G., NBL-247 (April 1969), p. 46.
2. Yuster, H. G. and Mullin, H. R., NBL-210 (June 1964), p. 21.

GETTER SYSTEM FOR IMPULSE HEATER GLOVED BOX

T. Tarr and C. G. Goldbeck

The method of determining oxygen by impulse heating, developed by Goldbeck, Turel, and Rodden,¹ involves sample loading in an inert atmosphere enclosure. A logical extension of the inert atmosphere enclosure is a gas purifying and recirculation system designed to remove water, carbon dioxide, and oxygen from the helium atmosphere. The system used in this work is a modification of one described by Waterbury, Smith, and Hansel.² In this system copper turnings heated to 600°C serve as the oxygen getter, and molecular sieve 5A and drierite are used as the desiccant and carbon dioxide trap, Figure 1.

Initially the gloved box is simultaneously filled and emptied, using the house vacuum to remove the gaseous contents and having pure tank helium flowing into the box. Then the filling and emptying process is stopped. At this point the helium atmosphere is being recirculated through the purification system and the apparatus is ready for a blank determination.

A blank as low as 4 μ g. of oxygen can be obtained. The gettering system also keeps the oxygen level at a constant level from one analysis to the next. Once established, the blank values are very stable despite the fact that Evans³ has reported the permeation rate of oxygen through latex gloves to be very rapid.

REFERENCES

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3. Evans, F. P., AWRE-O-56/57 (January 1958).

FIGURE 1. GAS PURIFYING AND RECIRCULATING SYSTEM.

A COMPUTER CONTROLLED ISOTOPE RATIO MASS SPECTROMETER WITH DRY REED RELAYS

L. C. Nelson, Jr. and R. J. Hemmer

A standard PDP-8 (Digital Equipment Corporation, DEC) computer is being used, along with a relay-driver buffer interface (DEC), circuit card mounted dry reed relays (Grigsby-Barton, Inc.), and an AF01A (DEC) analog to digital (A/D) converter, to control the data acquisition from a thermionic emission isotope ratio mass spectrometer. This system is used because the isotope masses to be measured are known and can be preselected by controls on the mass spectrometer.

Eleven relays, under operator control, select 5 mass peaks and 6 background positions (1 above and 1 below each peak) by controlling the magnet power supply. Another set of relays adjusts the 8 range positions of the vibrating reed electrometer (VRE). Data are collected from the VRE by the 12-bit A/D converter. All data are collected in batches of 100 to obtain adequate precision.

There are two computer programs at present, one to analyze boron and the other to analyze uranium, the latter measurements involving 2, 4, or 5 peaks. Calculations utilize the floating point program, and the internal precision of the mass spectrometer is estimated by a standard deviation subroutine.

The analytical results show no evidence of any noise or other interfering effects. They are reproducible with variations of 1 digit in the third decimal place. The system appears to be practical, reliable, and flexible. Furthermore, it allows other uses of the computer on an alternating basis.

A more complete description of the system has been published elsewhere.¹

REFERENCE

1. Digital Equipment Computer Users Society, Spring Symposium, May 12, 13, 1969, p. 201

A SYMMETRICAL CYLINDRICAL ROTATING STEP SECTOR

H. G. Yuster

A cylindrical step sector having the advantages of simplicity of construction and strength is described. Mathematical treatment to aid in the construction is given. The sector is easily machined from black non-reflecting plastic (Tenite). It is relatively free of vibration at high speeds. Graphical interpretations of plate calibration data are presented.

A complete report of this work is being published elsewhere.

A DARKROOM TIMER

H. G. Yuster and R. L. Graff

Desirable features of a timer for spectrochemical photographic use are the applicability to be reset in total darkness and reliability under repetitive use. Most timers recommended for darkroom use are of the ratchet and bell mechanical type and require some light for resetting the timing cycle. This type of timer has a high casualty rate due to the wearing of the ratchet causing failure to start or failure to complete the cycle of pre-set time. After having numerous mechanical timers become inoperative in a relatively short time, it was decided to construct an electrical timer that did not have the defects of the mechanical type.

A timer was constructed consisting of two 120-sec. electrical clock timers. Each clock timer contained a 120-v. AC motor and the necessary switching for placing power on an audible section. The audible section consisted of a 24-v. AC buzzer and the necessary stepdown transformer for operation from line voltage.

A circuit diagram of the timer is shown in Figure 1. In performance, the following sequence of events take place when switch S is in the position as drawn. To start, switch S_2 is depressed, relay R is energized and the normally open contact of the relay is connected with the unconnected side of the line. The relay remains in a locked position through S_1 even when the push button starting switch is released. Power is simultaneously placed on the clock motor in timer No. 1. At the end of the pre-set time, the microswitch in the timer connects power to T and the buzzer sounds the end of time. Pressing the push button S_1 releases the power, allows the clock to reset, and places the timer on standby for the next timing cycle. If more than 120 sec. are needed for timing purposes, S may be thrown in the other direction to place the timers in series. The total time is then the sum of the preset time on both timers.

The timer could be simplified by the use of only one timer covering a longer time period, but versatility is increased if two timers are used. For example, different timing of plate or film development and fixing may be obtained by the use of S which can be easily switched in total darkness.

- P 120 v. AC input power
- F 0.4 amp. slo-blow fuse
- R 120 v. AC SPST relay
- S₂ Normally open push button switch
- S₁ Normally closed push button switch
- S DPDT toggle switch
- T₁, T₂ 120 sec., 120 v. AC timers, R.W. Cramer Co.
1. Timer motor
2. Timer motor and switch common
3. Normally open switch contacts
- T 120 - 28 v. stepdown transformer
- B 28-v. buzzer

FIGURE 1. CIRCUIT DIAGRAM OF TIMER