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**ANNUAL PROGRESS REPORT FOR THE
PERIOD JULY 1971—JUNE 1972**

October 1972

New Brunswick Laboratory (AEC)
New Brunswick, New Jersey

MASTER

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UNITED STATES ATOMIC ENERGY COMMISSION

ANNUAL PROGRESS REPORT FOR THE PERIOD
JULY 1971 THROUGH JUNE 1972

AEC Research and Development Report

Carleton D. Bingham, Director

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October 1972

NEW BRUNSWICK LABORATORY

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ABSTRACTS

Automatic Titrimetric Determination of Uranium by the Constant Current Generation of Vanadium(V)

An automatic instrument for determining uranium based upon the constant-current generation of vanadium(V) was designed and constructed. Some evaluation studies of the instrument are presented.

Automatic Instrument for the New Brunswick Laboratory Titrimetric Method for Determining Uranium — A Continuing Evaluation

The precision and accuracy of the results obtained with the automatic instrument for determining uranium based upon dichromate titration have been determined for an additional 7-month period. No serious maintenance problems arose during this period.

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

The elimination of manganese interference with the New Brunswick Laboratory titrimetric method of determining uranium by fuming the sample with sulfuric, perchloric or phosphoric acid was found to be successful only when nitrate was initially present in the sample.

The Effects of Impurities on the Determination of Uranium by the New Brunswick Laboratory Titrimetric Method

A systematic study of the effect of impurity cations and anions on the New Brunswick Laboratory titrimetric method of determining uranium has been initiated. In the present report the effects of copper, titanium, cobalt, nickel, cerium and samarium are described.

Dissolution of Silicon Carbide-Coated Uranium-Thorium Carbide Fuel Pellets

Dissolution of silicon carbide coated uranium-thorium carbide fuel pellets can be accomplished by fusion with a sodium carbonate-sodium chromate mixture after an ignition step to remove a graphite outer coat.

Dissolution of Silicon Carbide Coated Uranium-Thorium Carbide Fuel Pellets — Ignition and Sodium Carbonate and Sodium Bisulfate Fusion Procedure

The New Brunswick Laboratory procedure for dissolving silicon carbide-coated uranium-thorium carbide fuel pellets by ignition, sodium carbonate fusion, and sodium bisulfate fusion is described.

Determination of Free Carbon in Boron Carbide - A Progress Report

Preliminary tests are described on the development of a method to determine free carbon in boron carbide by the selective oxidation of the carbon with an oxygen plasma oxidizer.

Preliminary Evaluation of a Rapid Mass Spectrometric Method of Determining Boron Isotopic Abundance in Boron Carbide

A procedure involving the formation of the charge material sodium tetraborate directly on the mass spectrometer filament was evaluated for the isotopic analysis of boron in boron carbide. The procedure shows a standard deviation of 0.004 in the $^{11}\text{B}/^{10}\text{B}$ ratio and a bias of +0.24% when compared to the conventional method of preparing the charge material based on a sodium carbonate fusion, ion-exchange separation of the boric acid, and treatment of the boric acid solution with sodium hydroxide.

A Current Evaluation of the Isotope Dilution Mass Spectrometric Procedure for Determining Uranium and Plutonium

The precision and accuracy of the New Brunswick Laboratory isotope dilution mass spectrometric procedure for determining uranium and plutonium concentrations have been determined under routine operating conditions over an extended period of time. The relative standard deviation of the uranium and plutonium results are 0.40 and 0.20%, respectively; the accuracy, expressed as the relative average difference between the prepared and found values, are +0.040% and +0.035%, respectively, with no bias at the 95% C.L.

An Improved Vacuum Lock for a Thermal-Ionization Source Mass Spectrometer

The vacuum lock designed and constructed by the New Brunswick Laboratory for use on each of two thermal ionization mass spectrometers was modified for operation on a tandem instrument used chiefly for the analysis of plutonium and uranium-233 samples.

Preparation of Uranium Charge Material for Mass Spectrometric Isotopic Analysis

Improved procedures for the separation of uranium for mass spectrometric isotopic analysis are described. These procedures are more rapid and require less handling of the sample than those previously reported.

Spark-Source Mass Spectrometric Determination of Impurities in Uranium Hexafluoride in the Gaseous Phase

A method for the spark-source mass spectrometric determination of impurities in uranium hexafluoride is being developed. The method will involve the introduction into the instrument of the sample in the gaseous phase.

Secondary Controlled-Potential Coulometric Determination of Chromium(VI) with Iron as an Intermediate

The controlled-potential coulometric reduction of chromium(VI) was studied. A method was developed for the reduction that involves a secondary coulometric technique with iron as an intermediate.

The Effect of Residual Oxygen and Electrode Treatment on the Controlled-Potential Coulometric Determination of Iron

The adverse effects of residual oxygen and nitric acid treatment of the platinum working electrode on the controlled-potential coulometric determination of iron were studied. With the recommended method of deaeration and freshly prepared electrolyte solutions, these difficulties are eliminated.

Separation of Antimony From Uranium by Collection on Manganese Dioxide - An Evaluation

A procedure reported in the literature for the separation of antimony from uranium and other elements by collection on a manganese dioxide precipitate prior to the spectrophotometric determination of antimony was evaluated. Only about 45% recovery of the antimony was obtained and bismuth, which interferes with the spectrophotometric measurement, was not separated.

Atomic Absorption Spectrophotometric Determination of Impurities in Elemental Boron

An improved atomic absorption spectrophotometric determination of impurities in elemental boron is reported. In this procedure, the boron is removed by volatilization as the methyl ester from the solution prepared by dissolving the sample in mixed acids. The removal of the boron results in greater sensitivity in determining many impurity elements.

Evaluation of a Deuterium-Arc Background Corrector for the Atomic Absorption Spectrophotometric Determination of Impurities in Uranium Solution - A Progress Report

A Perkin-Elmer Deuterium-Arc Background Corrector was briefly evaluated by analyzing uranium standards for impurities. The Corrector improved the results for certain impurities and had little effect on others. More comparisons are planned in future work.

Determination of Uranium-235 Isotopic Abundance with the Interference Spectrometer - A Progress Report

Studies have been initiated on the determination of the ^{235}U abundance by means of the interference spectrometer. An empirical equation for the calculation by a computer of ^{235}U abundance up to 10% from the ^{235}U and ^{238}U recorder trace peak heights was developed.

Cobalt as a Spectrochemical Internal Standard

The reliability of cobalt as an internal standard for the

spectrochemical determination of impurities in uranium and thorium was studied. Despite the fact that cobalt volatility decreases with an increase in total impurity concentration, the determination of most impurities is helped by its use.

Determination of Plutonium and Uranium in Plutonium Dioxide-Uranium Dioxide-Dylene Mixtures

Analyses of synthetic PuO_2 - UO_2 -Dylene (polyethylene) mixtures for uranium and thorium indicate that the determination of these elements in actual samples of this type would be satisfactory.

Adjustment of Plutonium Oxidation State by Ferrous and Dichromate Ion Treatment - A Preliminary Study

A study was made of the adjustment of plutonium in solution to the plutonium(IV) oxidation state by treatment with ferrous and dichromate ion and amperometric or potentiometric detection of the changes involved at each step.

Controlled Potential Coulometric Determination of Plutonium After Ion-Exchange Separation in Mini-Columns

A controlled-potential coulometric procedure for determining 5-mg quantities of plutonium was developed involving the use of mini-columns for the ion-exchange separation and a novel method of adjusting the plutonium to the plutonium(IV) oxidation state prior to separation.

Detection of Uranium in Ion-Exchange Effluents

A colorimetric test with a minimum of pretreatment was developed to detect uranium in ion-exchange effluents.

Acid Dissolution of Samples in Micro-Kjeldahl Flasks - A Progress Report

The applicability of micro-Kjeldahl flasks for the nitric acid dissolution of plutonium samples was studied with U_3O_8 as the simulated plutonium material. When the flasks were equipped with condensers to promote refluxing, dissolution was much faster than in open beakers, and less acid was necessary.

Safe Storage of Plutonium Solutions

The New Brunswick Laboratory plutonium solution storage assembly was evaluated with respect to adequate venting of hydrogen which is produced as a product of radiolysis. Various size vents were considered and the rate at which hydrogen can be safely released from each was calculated.

AUTOMATIC TITRIMETRIC DETERMINATION OF URANIUM BY THE CONSTANT CURRENT GENERATION OF VANADIUM(V)

C. G. Goldbeck and M. W. Lerner

The basic New Brunswick Laboratory (NBL) titrimetric method of determining uranium involves the reduction of uranium to uranium(IV) with ferrous ion in a phosphoric acid medium, oxidation of the excess ferrous ion with nitric acid and molybdenum catalyst, addition of vanadyl ion and dilution of the phosphoric acid medium with water, and finally potentiometric titration of the uranium(IV) with standard dichromate solution.¹ This procedure has been automated at NBL^{1,2} Recently, a 25-month evaluation of this Dichromate Titrator has been made.³

Another NBL version of this general titrimetric method involves the titration of the uranium(IV) with vanadium(V).⁴ In this vanadate titration procedure, vanadyl ion is not added as such, but it is formed immediately on adding the first quantity of titrant, and it has the same beneficial effect on the end point. Additional NBL studies⁵ indicated that the vanadium(V) titrant can be coulometrically generated at constant current. This new type of coulometric titration was found to be simpler than the previously reported procedure for uranium of Goode, Herrington and Jones⁶ involving the reduction to uranium(IV) by titanium(III), the reaction of uranium(IV) with iron(III), and the titration of the iron(II) with electrogenerated cerium(IV).

The present report describes the automation of this coulometric procedure together with the reliability data obtained to date with the instrument.

EXPERIMENTAL

Reagents and Apparatus

The reagents are identical to those described in reference (1) Part II except that the diluent is 1% H_2SO_4 containing 0.025M vanadyl sulfate.

The Constant Current Titrator has several components in common with the Dichromate Titrator.¹ For example, the Fisher Titralyzer turntable and elevator unit is used as before. Also, two solenoid valves to control the flow of gravity-fed reagents and three pumps to control the addition of the two remaining reagents and the rinse water are identical in both instruments. The reagent addition and rinsing functions are described adequately in reference (1) Part II.

The block diagram of the titrator is shown in Figure 1. The components that differ from those in the instrument previously reported are described in some detail in the following paragraphs.

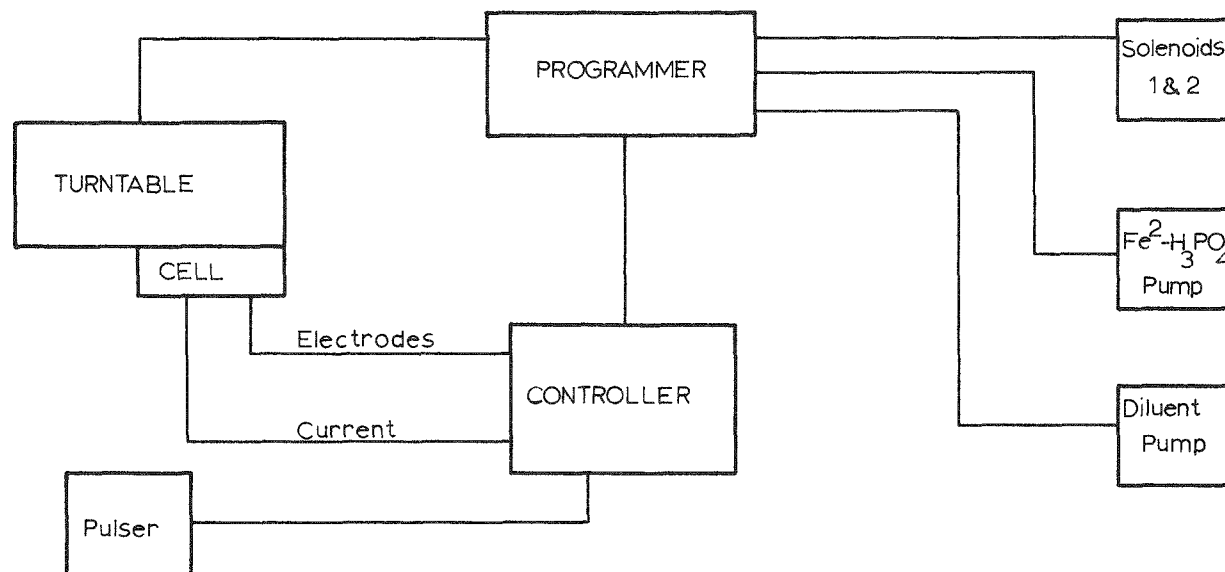


FIGURE 1. BLOCK DIAGRAM OF CONSTANT CURRENT AUTO-TITRATOR

The auto-titrator is composed basically of 3 main units plus their peripheral components. The 3 units are (1) the timer-programmer; (2) the main controller; (3) the elevator and turntable assembly. An external pulse generator, the solenoids and the pumps comprise the peripheral components.

Timer-Programmer. This unit is identical to the unit² used to replace the mechanical-cam type originally on the Dichromate Titrator. It is an Agastat Programmer Model 2912 made by the Amerace-Esna Corporation. It has 12 step functions and 3 adjustable time base units, any one of which can be selected for each step. The programmer has a plate mounted on the back with receptacles for powering the solenoids and pumps directly in their proper sequence. There are also receptacles on the plate for connections to the controller and to the elevator and turntable assembly.

This programmer controls the timing of the delays and the durations of the reagent additions much more accurately than the mechanical unit previously used.¹ In addition, it resets for the next cycle immediately after the completion of a titration. The mechanical type must wait for some minutes before a reset occurs. Thus, a time savings of 1 to 4 min per titration is made with this programmer.

To avoid splattering of reagents by the stirrer, the stirring was programmed to start only after the addition of the sulfamic acid and the ferrous- H_3PO_4 reagents rather than before any reagent addition is made as with the original Dichromate Titrator.¹ This same feature was used in later modification of the Dichromate Titrator.² As discussed below, a problem with the analysis of uranium-thorium samples shows up with this stirring program.

The sequence of a complete cycle and the time for each step are shown in the time-base chart, Figure 2. Also shown are the contacts used on the programmer load switches for each step. The wiring diagram of the switch functions are shown in Figure 3.

Main Controller. The main controller has 7 sub-assemblies, Figure 4.

(1) Constant Current Source, CEA Division of Berkleonics, Incorporated, Model 6D300Y501R unit, adjustable from 0 to 500 mA.

(2) Electrometer Amplifier, Analog Devices, Model 311J.

(3) Sense Meter, API Instrument Company Compack Controller I. This meter has a low and high set point. It is wired so that its zero is an offset voltage of -400 mV. This offset is adjustable. During a titration the meter registers a range of 250 mV, full scale thus being -650 mV. The low set point shuts off the continuous flow of current to the cell. A pulse from an external pulse generator then is fed to a relay driver (4).

(4) Relay Driver, Figure 5.⁷ Upon being pulsed, this unit drives its output relay, RL2, Sigma Instruments Incorporated, Model 5R 1000 S S1L, which in turn drives the output relay RLI, 3 PDT 10 A 12 V dc, through the low set point relay of the sense meter. The

FIGURE 2: 18 STEP
MULTIPLE TIME-
BASE CHART

STEP NUMBER CONTROL TO ADVANCE DWELL TIME IN SECONDS DESCRIPTION OF OPERATION				CIRCUIT DESCRIPTIONS																				
				10 Sec.	100 Sec.	10 Min.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	
				NO	NO	NO	NO	NO	NC	NO	NO	NO	NO	NC							NO OR NC CONTACTS			
				CIRCUIT CODE																				
1		7	add sulfamic acid	X			X								X						1			
2		33	add Fe ⁺² -H ₃ PO ₄		X		X								X						2			
3		20	mix (slow stirring start)	X																	3			
4		16	add HNO ₃ -molybdate	X			X														4			
5		180	mix (slow) continues			X															5			
6		11	add diluent	X				X		X											6			
7		5	mix (high-speed stirring)	X					X	X											7			
8		-	titrate	X					X	X	X										8			
9		5	print integrated time	X								X			X						9			
10		5	reset timer	X									X		X						10			
11		5	advance turntable	X										X	X						11			
12		-	start new run	X											X						12			
13																					13			
14			X = plugs placed in																		14			
15			programmer drum at																		15			
16			these points																		16			
17																					17			
18																					18			
TOTAL				10 Sec.	100 Sec.	10 Min.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	

TOTAL
DWELL TIME

SEGMENT GUIDE

10 SEC. 100 SEC. 10 MIN. A B C D E F G H I J K L M N O P Q

NO OR NC CONTACTS

CIRCUIT CODE

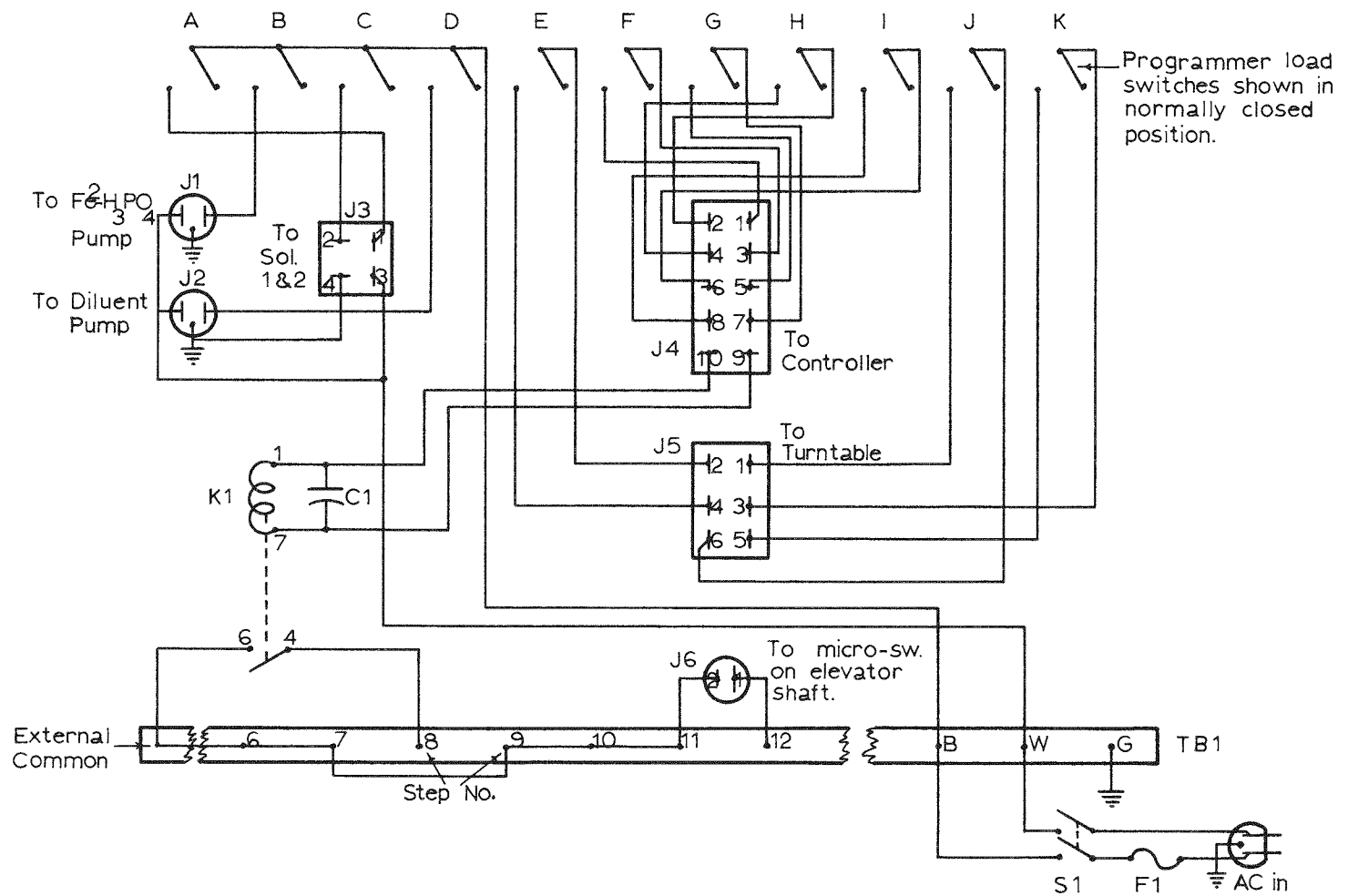


FIGURE 3. PROGRAMMER SWITCH FUNCTION WIRING

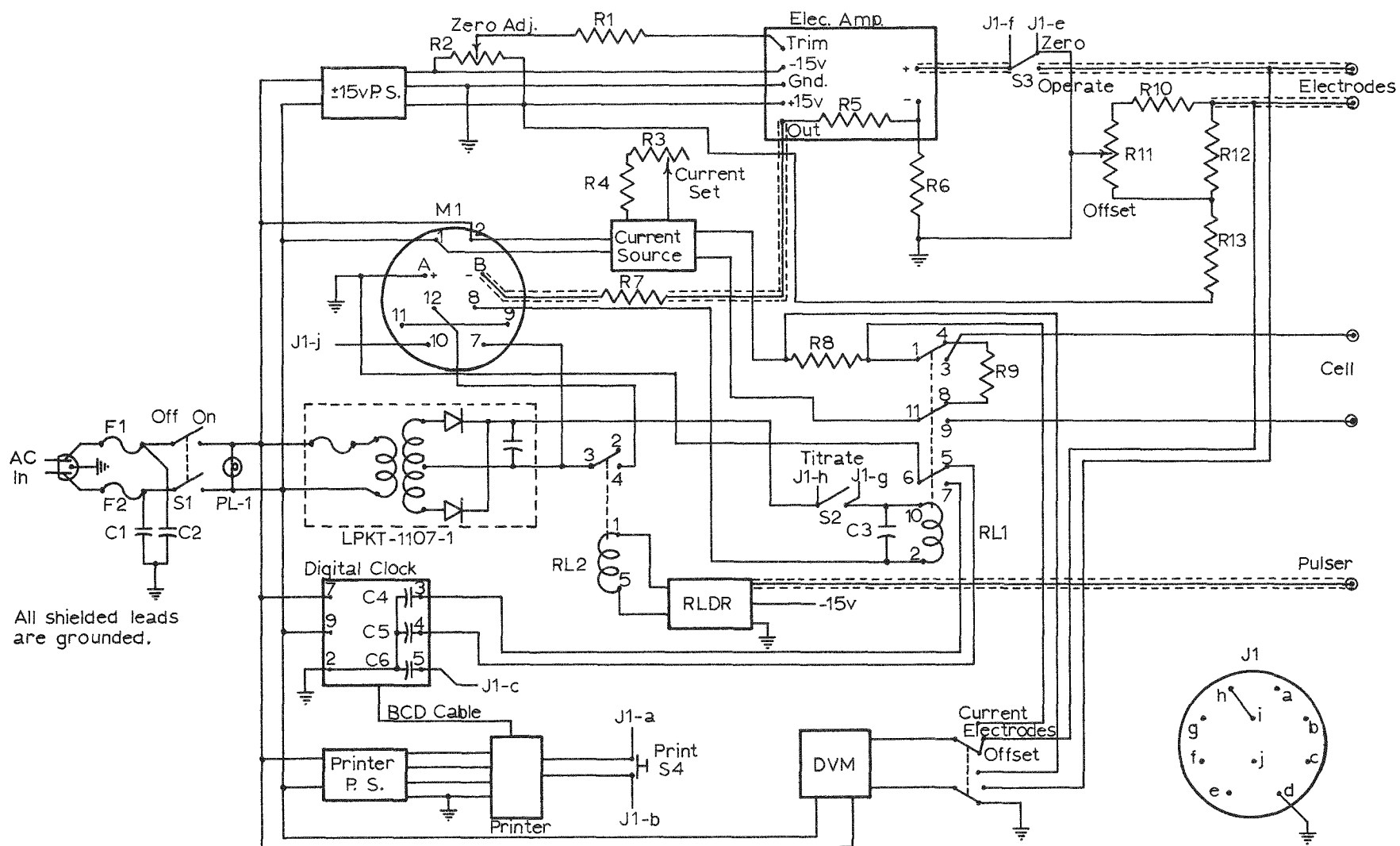


FIGURE 4. CONSTANT CURRENT AUTO-TITRATOR CONTROLLER

Elec. Amp.	- Electrometer amplifier, Analog Devices, Model 311J	F1,2	- 1A, 250V 3AG
$\pm 15V$ P.S.	- 15V dc at 50 mA power supply, Analog Devices, Model 904	J1	- Amphenol 18-1S
Current Source	- CEA Division of Berkleonics, Incorporated, Model 6D300Y501R, variable 0-500 mA	R1	- 1 Meg 1%
M1	- Sense meter, API Instrument Company, Compack Controller 1, Model 503-K	R2	- 10K, ten-turn Helipot
Digital Clock	- Electronics Research Company, Model 26215, 999.99 sec	R3	- 100 ohms, ten-turn Helipot
Printer P.S.	- Printer power supply, Practical Automation, Part No. 6-26	R4	- 360 ohms 1/2w 5%
Printer	- Practical Automation, Model CMMP-6	R5	- 950 ohms 1%
DVM	- Digital voltmeter, Weston, Model 1294	R6	- 50 ohms 0.05%
RLDR	- Relay driver	R7	- 495K 0.05%
LPKT-1107-1	- Lambda power supply kit 12V dc at 1.0 A	R8	- 5 ohms 0.05%
C1,2	- 0.01 μ f 400V dc	R9	- 15 ohms 5w
C3	- 0.068 μ f 400V dc	R10,12	- 47K 1/2w 5%
C4,5,6	- 0.1 μ f 75V dc	R11	- 100K ten-turn Helipot
		R13	- 430K 1/2w 5%
		RL1	- 3PDT 10A 12V dc
		RL2	- Sigma 5R 1000 S Sil

FIGURE 4 (Continued). CONSTANT CURRENT AUTO-TITRATOR CONTROLLER

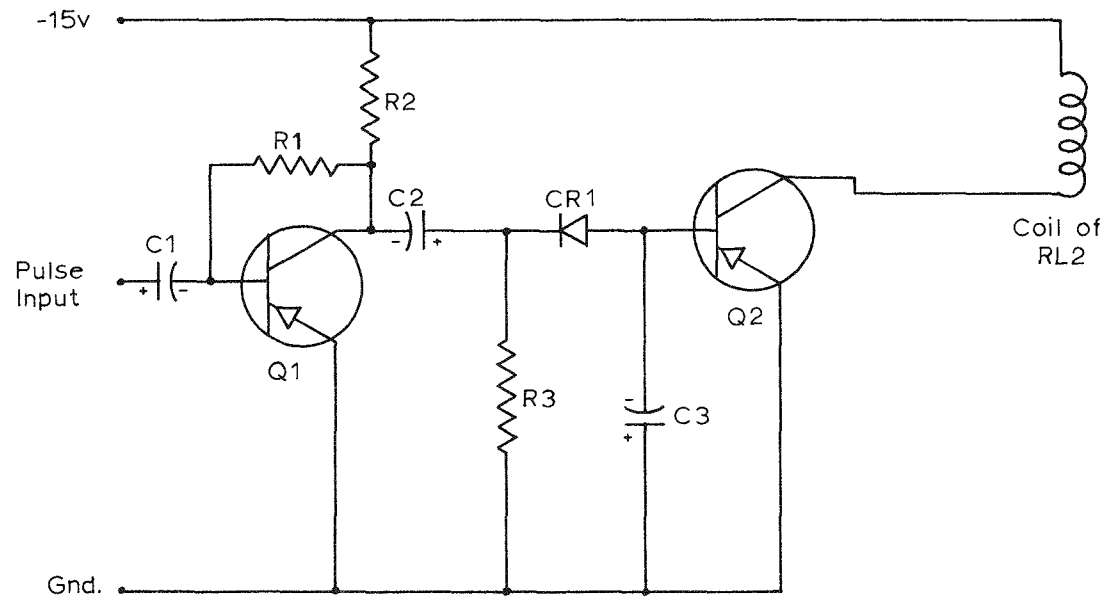


FIGURE 5. RELAY DRIVER

pulsing continues until the high set point is reached, and the current is then shut off by the high set point relay in the meter to end the titration.

(5) Digital Clock. The clock is an Electronics Research Company, Model 26215 unit reliable to \pm last digit of display or \pm 0.01 sec. This clock measures the total accumulated time during which the current is applied to the cell. The BCD output of the clock is connected to a miniprinter.

(6) Printer, Practical Automation No. 6MMP-6. The printout is accomplished by using the relay driver output relay to drive relay K-1 of the Programmer which moves step 8 to the print step, number 9.

(7) Digital Volt Meter, Weston, Model 1294. This DVM on the controller measures the offset potential, the electrode potential, and the current.

The cable connections between the Controller and the Programmer are shown in Table I.

TABLE I
PLUG CONNECTIONS FOR CABLE BETWEEN
CONTROLLER AND PROGRAMMER

<u>Amphenol Plug No. 18-1P to Controller, Letter</u>	<u>Jones Plug to Programmer, Number</u>
A	2
B	4
C	6
D	8
E	3
F	1
G	7
H	5
I	10
J	9

Turntable-Elevator, Fisher Scientific Company Titralyzer. The turntable holds twelve 400-ml tall-form beakers. The elevator is modified somewhat. For example, the stirrer motor power and speed is controlled by the Programmer. The power required to raise the elevator and position a new sample is routed through the programmer. These connections are shown in Figure 6. A microswitch located on the elevator motor shaft activates the programmer from step 12 to step 1 to begin a new cycle.

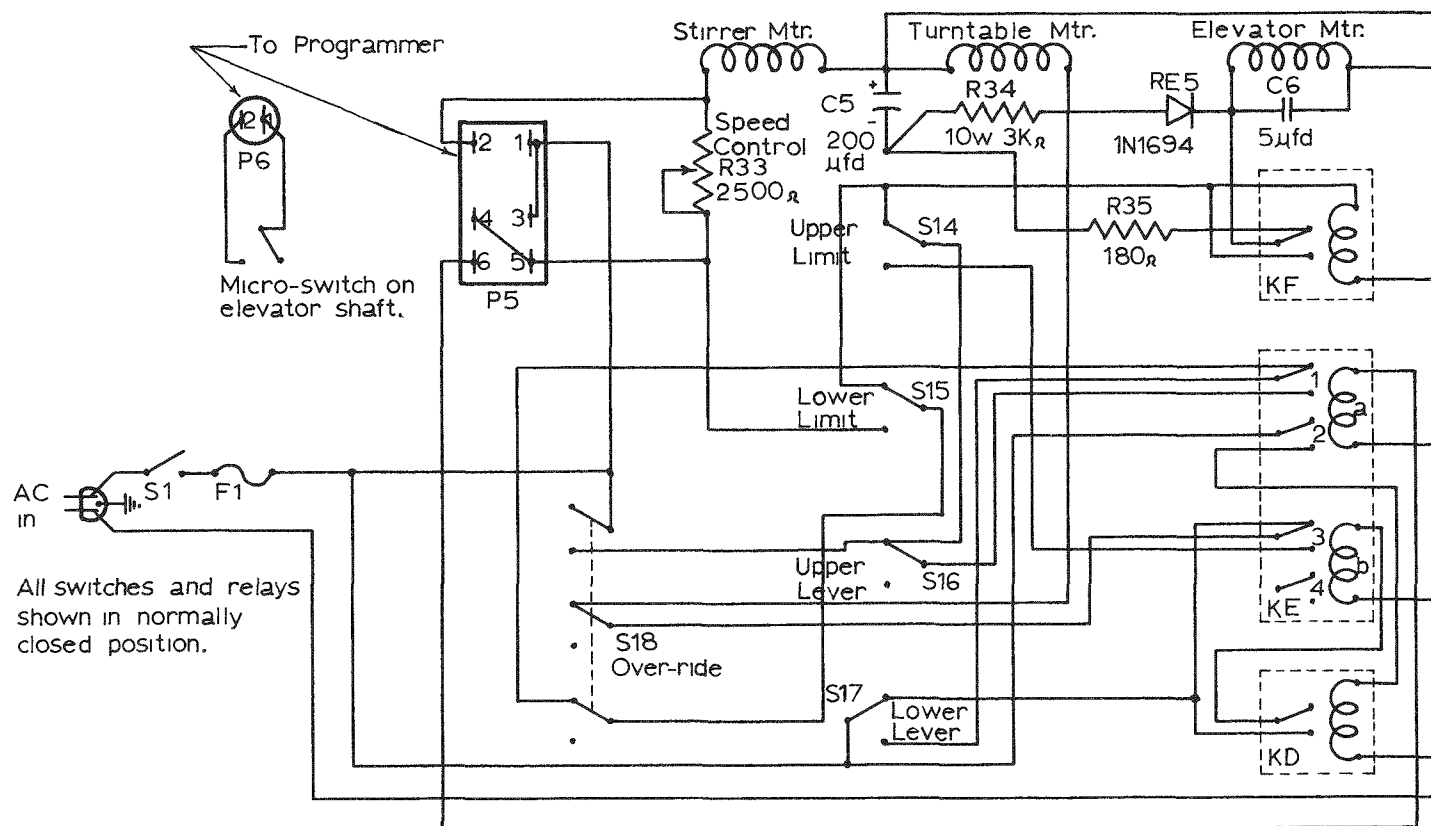


FIGURE 6. TURNTABLE ASSEMBLY WITH MODIFICATIONS

The annular ring for rinsing the electrodes, delivery tube tips and stirrer shaft together with the microswitch-straight cam arrangement for the activation of the rinsing, all of which are placed on the elevator, are identical to those on the Dichromate Titrator.¹

The elevator head of the Titralyzer is replaced by a 7/8-in. thick piece of Plexiglas with holes drilled for the electrodes, the reagent delivery tube tips and the stirrer water shaft as shown in Figure 7. Set screws at each hole, except that for the indicating electrode, keep the electrodes and tips firmly in position. A snug fit keeps the indicator electrode from shifting.

Electrodes. The generator electrode is a cylindrical platinum gauze electrode 4.8 cm long and 5.3 cm in diameter. The surface area is calculated to be 190 cm². The isolated counter electrode is made of a glass tube 1.3 cm o.d. and 14 cm long with a medium glass frit and agar plug at the lower end. The tube is nearly filled with dilute H₂SO₄ in which is immersed a coil of stout (14 gage) platinum wire. The reference electrode is a saturated calomel electrode (SCE), and the indicator electrode is a straight piece of the 14-gage platinum wire.

Procedure

With the turntable holding beakers containing samples, the reagent bottles filled, the programmer set to position 12, the current generator adjusted to the desired current level, the pre-selected potentials indicated on the meter of the current controller, the elevator directly over an empty position in the turntable, and the elevator control on "UP", the following operations will occur when the elevator is set to "AUTO":

PIN-12 (Programmer index number) - the turntable turns until a beaker is in position under the elevator head, and the elevator head drops until the electrodes, stirrer and feed tips are in the correct position;

PIN 1 - 5 ml of sulfamic acid reagent enters;

PIN 2 - 45 ml of ferrous sulfate-H₃PO₄ reagent enters;

PIN 3 - the stirrer starts at low speed;

PIN 4 - after 30 sec, 10 ml of the HNO₃-Mo reagent enters;

PIN 5 - a delay of 3.2 min occurs;

PIN 6 - 160 ml of diluent enters;

PIN 7 - the fast stirrer speed begins; the electrodes are activated;

PIN 8 - the titration begins;

PIN 9 - the potential reaches the selected cut-off point and the printer records the time on the tape;

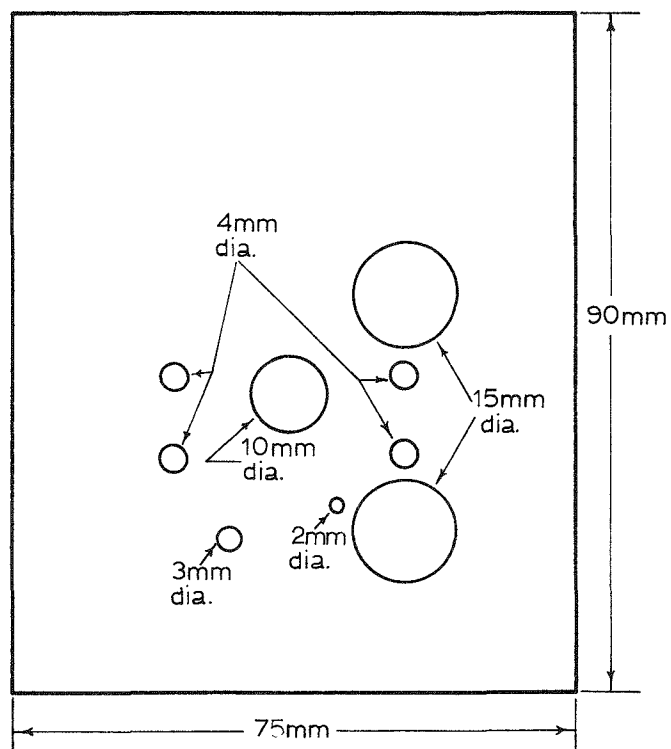


FIGURE 7. ELEVATOR HEAD

PIN 10 - the timer resets to zero; (the electrodes are disconnected);

PIN 11 - the elevator rises; the turntable turns to next beaker.

RESULTS AND DISCUSSION

Stability of the Uranium(IV)

In analyzing standard uranium solutions with the manual coulometric procedure before the automatic instrument was completed, a relative standard deviation (RSD) of 0.062% and a relative difference from the prepared value of -0.023 ± 0.048 (95% C.L.) was obtained on a typical set of 9 analyses. These latter values showed that no bias existed in the procedure although the average difference was negative.

After construction of the automatic instrument was completed, subsequent analysis of literally hundreds of standard samples indicated that a small negative bias did in fact exist. It was eventually found that this error was caused by some slight air oxidation of the uranium(IV) despite the fact that the titration was generally completed within 7 min, the time previously determined to be available for the normal dichromate titration without loss of uranium(IV).¹ Tests revealed that automatic titrations as short as 3 to 4 min gave small but detectable negative errors. Obviously, prolonged pulsing times aggravated the error greatly.

Two precautions were then taken. Firstly, the initial cut-off potential was carefully adjusted at the beginning of a series of analyses so that no more than about 10 pulses were needed for the completion of the titration. Secondly, the diluent was cooled to $< 10^{\circ}\text{C}$ in an ice bath. Under these conditions, a typical set of weighed standard solutions gave differences from the theoretical values that tested to be insignificant. Analyses of hundreds of such standards and samples of various types consistently gave results with precisions and accuracies within 0.1%.

Generating Electrode

As indicated in reference (4), the initial manual work was carried out with both an expanded gold and a platinum-gauze generating electrode. With the gold electrode, large samples, > 200 mg uranium, caused a black deposit to form on the electrode and cell walls, and high results were invariably obtained. No such deposit occurred with the platinum electrode which was used with the automatic instrument because it was appreciably sturdier in construction.

However, whenever more than four consecutive large samples (> 190 mg), were analyzed by the automatic instrument with the platinum electrode, again the results started to show large positive errors. This electrode behavior could be checked quickly by applying a voltmeter between the reference electrodes and the generating electrode: when the voltage stayed below 1.4V no trouble would occur. When the voltage crept up to this value and beyond, the results would become very high.

That this phenomenon was caused by a surface factor of the generating electrode was shown by the fact that a HNO_3 wash and flaming restored the electrode to its efficient behavior. However, it was found that a simple dip in the ferrous- H_3PO_4 reagent diluted 1:4 for even a few minutes restored its activity more efficiently. Routinely, then, the electrode was stored overnight in this solution. After this treatment, any number of large samples could be analyzed without abnormally high results occurring.

Analysis of U-Th Solutions

With the stirrer starting only after the addition of the ferrous- H_3PO_4 reagent, splattering is held to a minimum. However, one drawback to this arrangement exists. In the analysis of U-Th solutions, the addition of the H_3PO_4 without stirring causes the solution to gel and mixing does not occur. The uranium, then, does not get completely reduced before the HNO_3 -molybdate reagent enters. These tests were conducted with samples containing about 100 mg of uranium and about 1500 mg of thorium. With these quantities, the stirring should begin at the start of the reagent additions; essentially clear solutions result and reduction proceeds normally.

Current Level

A current of 300 mA, as was used with the manual technique, was relied upon on all the initial work. Later, when the possibility existed that there could be a slight loss of uranium(IV) with time, 500 mA was tried and found to be satisfactory. Typical data with the 500 mA current are shown in Table II.

In the analysis of U-Th solutions, it was found that samples containing only about 150 mg of thorium and 10 to 20 mg of uranium could be used without gel formation occurring from the lack of stirring before the addition of the ferrous- H_3PO_4 reagent. With these samples, a current of 100 mA was used, Table III. The results with these small samples appear to be somewhat high.

The ease with which the current level can be adjusted to give reasonable titration times for any one group of samples is an attractive feature of the coulometric titration. In effect, the titer of the oxidant can be changed by turning a dial.

TABLE II
DETERMINATION OF URANIUM AT 500-mA CURRENT

NBL Sample No.	Sample Type	Uranium, %		
		Prepared	"Automatic"	"Manual" ^a
EU-18454	UNH	-	51.27, 51.30, 51.17, 51.20	51.15
EU-18455	UNH	-	52.54, 52.57	52.51
		-	52.54, 52.54	52.51
EU-18457	Dissolver	-	1.133, 1.125, 1.133	1.121
EU-18456	Dissolver	-	0.5314	0.534
F-6657	U-Nb	1.300	1.304, 1.303, 1.304	1.300
F-6285	U-stainless steel	0.674	0.676, 0.677, 0.677, 0.677	0.674
EU-18156-1	UNH	-	52.52, 52.49, 52.50	52.50
EU-18157	Dissolver	-	1.296, 1.297, 1.300, 1.300, 1.299, 1.298, 1.298, 1.300	1.299
EU-18158	Dissolver	-	1.950, 1.946, 1.944, 1.945, 1.943	1.944
EU-18327	Dissolver	-	0.848, 0.846, 0.848	0.846
EU-18328	Dissolver	-	1.592, 1.590	1.587

a. results obtained by a manual dichromate titration.

TABLE III
DETERMINATION OF URANIUM IN URANIUM-THORIUM SOLUTIONS
WITH 100 mA CURRENT

NBL Sample No.	Uranium Titrated, mg	Uranium, %	
		"Automatic"	"Manual Dichromate"
EU-17962	10-12	5.64, 5.65, 5.64, 5.63	5.63, 5.65
EU-17971	9-11	4.00, 3.98, 3.99	3.95
EU-17969	14-15	3.64, 3.64	3.63, 3.62
EU-17970	20	4.55, 4.55	4.50
EU-17973	18-20	4.31, 4.31	4.27
EU-17974	14	3.50, 3.50	3.48

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Addendum to report NBL-265, page 20:

ACKNOWLEDGMENT

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AUTOMATIC INSTRUMENT FOR THE NEW BRUNSWICK LABORATORY
TITRIMETRIC METHOD FOR DETERMINING URANIUM -
A CONTINUING EVALUATION

M. R. Clickner

The automatic instrument¹ for the determination of uranium by the New Brunswick Laboratory (NBL) titrimetric method involving the reduction to uranium(IV) by ferrous ion in phosphoric acid, selective oxidation of the excess ferrous ion, and titration with dichromate, was evaluated in a previous report² after 18-months of continuous use. In the present report, the statistical data obtained from the analysis of standard solutions of uranium over an additional 7-month period are presented.

The data are listed in Table I along with the statistical evaluation for a typical set of analyses on standards carried out during one week of the previous 18-month period.

TABLE I
STATISTICAL EVALUATION OF CONTROL STANDARDS

<u>Number of Determinations</u>	<u>Period Covered</u>	<u>Relative Standard Deviation, %</u>	<u>Relative Average Difference from Prepared Value, %^a</u>
59	7/28/71 to 8/4/71	0.06	+0.009 \pm 0.016
137	1/3/72 to 7/24/72	0.07	-0.004 \pm 0.011

a. relative average difference \pm 95% confidence limits.

No serious maintenance problems arose during this 7-month additional period.

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1. Goldbeck, C. G., Lerner, M. W. and Rodden, C. J., NBL-252 Part II (July 1970), p. 26.
2. Clickner, M. R., Goldbeck, C. G. and Lerner, M. W., NBL-262 (March 1972), p. 17.

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

L. Z. Bodnar, J. M. Scarborough and M. W. Lerner

In a previous report,¹ it was shown that the interference of manganese in the New Brunswick Laboratory (NBL) titrimetric method² of determining uranium can be eliminated by evaporating a solution of the sample to dryness and fuming lightly with sulfuric, phosphoric or perchloric acid before the analysis. In the present study, it was found that the initial sample solution must contain nitrate ion for this pretreatment to be successful. The minimum amount of nitrate was established. A brief attempt was made to learn the mechanism by which the pretreatment eliminates the interference.

EXPERIMENTAL

Reagents and Apparatus

The reagents, apparatus and procedure are identical to those listed in references (1) and (2) except for the 0.05M vanadyl sulfate solution. In this study, 100 mg of solid vanadyl sulfate dihydrate is used in place of the 10 ml of 0.05M vanadyl sulfate in the dilution step.

RESULTS AND DISCUSSION

Elimination of Manganese Interference. In the determination of 120 mg of uranium, manganese(II) or (VII) in 2- to 25-mg quantities was shown to give negative errors up to about -0.30%.^{1,2} The effect of the manganese is erratic and often seems to be independent of the exact manganese concentration.

The interference can be overcome by evaporating the volume of sample solution containing HNO₃ taken for analysis to dryness, adding 5 ml of H₂SO₄ and fuming lightly, cooling, and adding 10 ml of water prior to carrying out the NBL titrimetric procedure.¹ Perchloric or phosphoric acid can replace the H₂SO₄.¹ Results obtained in the current study by applying this pretreatment to eliminate the manganese interference are shown in Table I. The same results are obtained with either manganese(II) or (VII).

It was established by oxidizing the manganese to purple manganese(III) by dichromate and subsequent spectrophotometry that the manganese was not simply volatilized by this treatment: the manganese was recovered completely.

TABLE I
ELIMINATION OF MANGANESE INTERFERENCES BY
EVAPORATION-FUMING TREATMENT

<u>Mn⁺² Present, mg</u>	<u>Relative Error, %^a</u>
0	+0.07, +0.05, +0.03
5	-0.05
10	+0.10, -0.01, +0.14, +0.02
15	+0.08, +0.09, +0.04, -0.03, +0.04, -0.01
25	+0.02, +0.00, -0.03

a. 100 mg uranium present; 10% HNO₃ present.

Tests were made to determine if the evaporation step or the fuming step could be dispensed with. Fuming solutions containing 100 mg of uranium and 20 mg of manganese with 5 ml of H₂SO₄ prior to the analyses gave the results shown in Table II. Likewise, evaporating similar solutions to dryness, and adding 5 ml of H₂SO₄ without fuming before the analyses gave the results which also are shown in Table II. It can be seen from the data¹ that both steps of the pretreatment are essential.

TABLE II
NECESSITY OF BOTH EVAPORATION AND FUMING STEPS
IN ELIMINATING MANGANESE INTERFERENCE

<u>Treatment</u>	<u>Mn⁺² Present, mg</u>	<u>Number of Analyses</u>	<u>Relative Error, %^a</u>
evaporation step only	15	6	-0.27, -0.38, -0.29, -0.29, -0.28, -0.40
fuming step only	20	6	-0.38, -0.48, -0.43, -0.34, -0.23, -0.36

a. 100 mg uranium present; 10% HNO₃ present.

Necessity of Nitrate Ion being Present in Evaporation Step. In the course of the studies made on the pretreatment steps for the elimination of the manganese interference, it was found that nitrate ion must be present during the initial evaporation to dryness. For example, if the uranium solution is first fumed with H₂SO₄, then manganese sulfate is added and the solution evaporated to dryness, and finally 5 ml of H₂SO₄ added and the solution fumed, the manganese still interferes as the data in Table III indicate.

TABLE III
PRETREATMENT IN THE ABSENCE OF NITRATE ION

<u>Mn⁺² Present, mg</u>	<u>Number of Analyses</u>	<u>Relative Error, %^a</u>
15	8	-0.32, -0.18, -0.24, -0.32, -0.27, -0.32, -0.25, -0.33

a. 100 mg uranium present.

Quantity of Nitrate Necessary in the Evaporation Step. To determine the minimum quantity of nitrate ion necessary to eliminate the interference, standard solutions of uranium were fumed with 2 ml H₂SO₄, then varying quantities of HNO₃ were added before the usual pretreatment of the solutions was carried out. The data are shown in Table IV. It appears that a 20-fold quantity of nitrate over the manganese on a mole basis must be present if the treatment is to be effective. If nitrate is absent in a sample, therefore, the addition of 1 to 2 ml HNO₃ must be made. This quantity should be sufficient for any reasonable amount of manganese that might be present.

TABLE IV
MINIMUM QUANTITY OF NITRATE ION NECESSARY TO
ELIMINATE INTERFERENCE FROM MANGANESE

<u>Mn⁺² Present, mmol</u>	<u>Nitrate Added, mmol</u>	<u>Relative Error, %^a</u>
0.00	32.0	+0.04
0.27	4.0	-0.21, -0.22
0.27	5.6	-0.15, -0.14
0.27	8.0	+0.03, +0.02
0.27	12.0	-0.01, +0.02
0.00	32.0	-0.04

a. 100 mg uranium present.

Mechanism of the Pretreatment

A brief attempt was made to learn why the pretreatment was effective in eliminating the interference. Spectrophotometric measurements were made of solutions containing uranium and manganese with and without added nitrate and to which the pretreatment was applied. The only difference in the absorption spectra was the existence of a broad, diffuse absorption band from 220 to 300 nm in the nitrate-containing solutions. Absorbance measurements made of the two types of pretreated solutions (with and without added nitrate) at each stage in the analytical procedure before the dilution and titration revealed no marked differences in the spectra.

The possibility exists that the pretreatment produces a nitrate-containing manganese complex ion. To test the stability of such a complex ion dilution, a solution containing uranium, manganese and nitrate was pretreated and diluted to 25 ml instead of 15 ml. After evaporation to 15 ml, the solution was analyzed and no interference from the manganese was found. It would appear, therefore, that the complex once formed is fairly stable. If manganese interferes by being oxidized by the HNO_3 -molybdate to an oxidation state capable of oxidizing uranium(IV), the complex may then be resistant to oxidation by the HNO_3 -molybdate.

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THE EFFECTS OF IMPURITIES ON THE DETERMINATION OF URANIUM
BY THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD

J. M. Scarborough

The interference of various impurity cations and anions on the New Brunswick Laboratory (NBL) titrimetric method have been reported.¹

Additional information is summarized herein on the effects of other selected metallic elements which may appear as impurities in uranium samples. This investigation, which is part of an extended effort to study the influence of impurities on the NBL titrimetric method, will continue until the effects of all potential impurities have been characterized.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus used in the NBL titrimetric method are described in reference (1).

Impurity Solutions

Copper, 0.2M HNO₃ containing 20 mg Cu/ml or an aqueous solution of CuSO₄ containing 10 mg Cu/ml.

Titanium, 85% H₃PO₄ containing 10 mg Ti/ml.

Cobalt, aqueous solution of CoSO₄·7H₂O containing 10 mg Co/ml.

Nickel, aqueous solution of Ni(NH₄)₂(SO₄)₂·6H₂O containing 10 mg Ni/ml.

Cerium, aqueous solution of Ce(NO₃)₃·6H₂O containing 10 mg Ce/ml.

Samarium, 2M H₂SO₄ containing 10 mg Sm/ml.

Procedure

Transfer weighed aliquots of uranium standard solution, each containing approximately 100 mg of uranium, to 400-ml beakers. Add appropriate amounts of impurities to the uranium standards. Proceed with the NBL titrimetric method in the usual manner.

RESULTS AND DISCUSSION

The data obtained from the titration of known amounts of uranium, to which various amounts of impurities were added, are shown in Table I. Although generally 5- to 50-mg quantities of impurities were tested, only the 50-mg results are given in Table I. Higher ratios were not investigated. None of the elements studied interfere with the titrimetric procedure when present in ratios of up to 50 mg of impurity to 100 mg of uranium.

TABLE I
EFFECT OF SELECTED IMPURITIES ON THE NBL TITRIMETRIC
METHOD FOR THE DETERMINATION OF URANIUM

<u>Impurity Element</u>	<u>Quantity of Impurity, mg</u>	<u>Quantity of Uranium Added, mg</u>	<u>Quantity of Uranium Found, mg</u>	<u>Relative Error, %</u>
Cu	50	102.19	102.22	+0.03
		101.62	101.67	+0.05
Ti	50	102.20	102.22	+0.02
		102.25	102.29	+0.04
Co	50	101.43	101.42	-0.01
Ni	50	101.43	101.48	+0.05
		101.66	101.61	-0.05
Ce	50	101.45	101.43	-0.02
		100.30	100.37	+0.07
Sm	50	101.00	101.04	+0.04
		101.36	101.36	0.0

REFERENCE

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

DISSOLUTION OF SILICON CARBIDE-COATED URANIUM-THORIUM CARBIDE FUEL PELLETS

C. E. Hedrick

Silicon carbide-coated fuel pellets are used in some high temperature reactors. These coatings have the advantages of low neutron cross section, good retention of fission products, and high mechanical strength, thermal conductivity and stability under intense neutron radiation.¹⁻⁴

Analysis of fuels of this type presents a problem because of the refractory nature of this silicon carbide coating. Many methods call for grinding the pellets and leaching the metals with acids.^{5,6} Other methods involve chemical attack on the coating. For example, selenium is reported to react with SiC at 300° to 700°C.⁷ A mixture of chromic and hydrofluoric acid together with a mercury catalyst has been studied as a means of removing silicon carbide coatings.⁸

Attempts to use these techniques to analyze silicon carbide coated fuels have been less than satisfactory. More promising has been the use of fused salts. Nitrate melts⁹ and a eutectic of lithium, sodium and potassium carbonate at 600°C have been studied.¹⁰

At the New Brunswick Laboratory (NBL) these coated fuel pellets have been dissolved routinely by a dissolution procedure involving ignition, a sodium carbonate fusion, and finally a sodium bisulfate fusion of the residue.¹¹ This procedure is generally satisfactory but very time-consuming.

Mixed salts have been tested recently at NBL for the dissolution. On the basis of speed of dissolution, absence of excessive reactivity towards platinum crucibles, freedom from reaction gasing, and ease of work-up after fusion, the best mixture found to date is a (1+10) sodium chromate-sodium carbonate mixture.

EXPERIMENTAL

Procedure

Ignite a 4.5 g sample of pellets in a 125-ml platinum dish for 6 hr over a blast burner. Cool the dish, add 20 g of sodium carbonate, and 2 g of sodium chromate, mix well, cover the dish and ignite again over the blast burner for 4 to 5 hr. Cool the dish, place it in a 800-ml covered beaker, add 500 ml of 20% (V/V) HNO₃, and allow the reaction to proceed to completion. Rinse and remove the platinum dish and cover.

Add 3 ml of 0.1N silver nitrate and 15 g of ammonium persulfate, and boil the mixture until the persulfate is decomposed

and fine bubbles no longer appear. Cool the solution and make it alkaline with freshly prepared NH_4OH . Filter the solution through 18.5-cm Whatman No. 41 paper. Discard the filtrate. Wash the paper with water, then acetone, and ignite it in a 125-ml platinum dish. To the residue add 50 ml HNO_3 , 25 ml HF and 25 ml HClO_4 . Evaporate the solution carefully to fumes of HClO_4 with a ribbed watch glass on the dish.

Cool the solution, dilute with 50 ml of 1N HNO_3 and wash the solution into a beaker. If an insoluble portion is present, filter the solution through 9.0-cm Whatman No. 42 paper, wash the paper with water, and ignite the paper in a 30-ml platinum crucible. Cool the crucible, add 0.2 g sodium nitrate and 2 g sodium carbonate, and fuse the mixture until a clear melt is obtained. Dissolve the cooled cake in 10 ml of 50% HNO_3 , add 5 ml of HF and 10 ml HClO_4 , and bring to HClO_4 fumes. Dilute the cooled solution with water.

RESULTS AND DISCUSSION

Many salt mixtures were tested. The mixtures included various combinations of sodium halides and sodium carbonate, sodium peroxide plus sodium carbonate or sodium hydroxide, sodium hydroxide plus sodium carbonate, and sodium sulfate alone and with sodium halides. Zirconium and nickel crucibles were used with many of these mixtures.

In general, sodium halides reduced the reactivity of sodium carbonate. Sodium hydroxide was less effective than the carbonate. Sodium peroxide caused violent reactions in mixtures containing more than 20% by weight, but below this concentration, it was less effective than sodium carbonate.

Sodium sulfate appeared to accelerate the reactivity of sodium carbonate. The fusion cakes, however, were difficult to dissolve because of the formation of insoluble thorium sulfate and free sulfur. Also, platinum vessels were appreciably attacked. Sodium nitrate plus sodium carbonate dissolved the fuel pellets fairly rapidly, but the flux gassed badly and the resulting foaming causes losses.

Sodium chromate was found to accelerate the dissolution of the fuel pellets with sodium carbonate without forming excessive gas and without attacking the platinum crucible badly. With the large amounts of chromium present, several different post-fusion procedures were tested for ease of recovery of uranium-thorium. Since treatment with H_2SO_4 or fusions with bisulfate are to be avoided because of the formation of insoluble chromic sulfate, in the most satisfactory procedure found, most of the chromium is removed by a preliminary persulfate oxidation and an ammonium hydroxide precipitation of the uranium-thorium and silica.

The recommended procedure was used to dissolve 7 samples of pyrocarbon and silicon carbide-coated uranium-thorium carbide beads, Table I. These samples were not riffled samples but were simple grab samples. The uranium determinations were carried out by the New Brunswick Laboratory titrimetric method. No difficulty was found in applying the dissolution procedure. The poor precision of the results in all probability arises from the inhomogeneity of the coatings.

TABLE I

ANALYSES OF PYROCARBON AND SILICON CARBIDE-COATED
URANIUM-THORIUM CARBIDE BEADS

Sample Weight, g	Loss on Ignition, %	Uranium Found	
		mg	g/g Sample
4.8170 ^a	34.22	207.45	0.04307
4.4950	33.17	204.61	0.04552
4.5483	-	210.15	0.04620
4.5775	-	208.89	0.04563
5.1140	32.32	224.89	0.04398
5.8928	32.44	276.73	0.04696
5.9189	32.25	276.72	0.04675

Average = 0.045445

relative standard deviation, % = 3.17

- a. thorium separated as oxalate prior to the uranium determination.

ACKNOWLEDGMENT

Thanks are due to Mr. Louis Bodnar for his determination of the uranium content of the processed samples.

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DISSOLUTION OF SILICON CARBIDE-COATED URANIUM-THORIUM
CARBIDE FUEL PELLETS — IGNITION AND SODIUM CARBONATE
AND SODIUM BISULFATE FUSION PROCEDURE

H. Zibulsky, J. S. Paller and T. J. Siddons

In another report,¹ a newly developed procedure is described for dissolving silicon carbide coated uranium-thorium carbide fuel pellets chiefly by means of ignition and a sodium carbonate-sodium chromate fusion. In the following report, the procedure currently in use at the New Brunswick Laboratory is described for comparison.

Procedure

Ignite up to a 10-g sample in an open 75-ml platinum dish for 5 hr or overnight in a furnace at 700°C. Cool and then fuse the sample with 35 g of sodium carbonate for 6 hr over a blast burner. Knock out the cooled fusion cake and wash the dish with water and a few drops of H_2SO_4 . Transfer the cake to a covered 1-l. beaker and add carefully 75 ml of HNO_3 and 100 ml of H_2SO_4 . When the reaction subsides, rinse the beaker cover, add 25 ml of HF, swirl, and heat the solution on a steam bath overnight.

Heat the solution, slowly at first, on a hot plate to fumes. While the solution is fuming, add HNO_3 dropwise to oxidize the carbon. Cool the solution, wash down the beaker sides with water, and again evaporate to strong fumes. Cool the solution, add about 700 ml of water, and dissolve the salts by stirring and cooling in an ice bath if necessary.

Filter the solution through a 18.5-cm Whatman No. 42 paper, collecting the filtrate in a 1500-ml beaker. Wash the precipitate with 1% H_2SO_4 adding the washing to the filtrate. Reserve the filtrate.

Ignite the paper in a 50-ml Vycor crucible at 700°C for 5 hr, then fuse the residue with up to 10 g of sodium bisulfate to get a clear melt. Place the cooled crucible in an 800-ml beaker containing about 300 ml of water and stir until the cake is loosened. Wash and remove the crucible. Dissolve the cake by stirring.

If the solution is not clear, filter it through 11-cm Whatman No. 42 paper, collecting the filtrate in one of the filtrate beakers. Ignite the paper, fuse the residue with about 1 g of sodium bisulfate, and dissolve the cooled melt as before.

Combine the filtrates. Add freshly prepared NH_4OH until the solution is ammoniacal, then add 15 ml in excess. Filter the solution through 18.5-cm Whatman No. 42 paper and wash the precipitate with freshly prepared 10% NH_4OH . Dissolve the hydroxides from

the paper with hot 1:1 HNO_3 into a clean beaker, finally washing the original beaker and paper with hot 10% HNO_3 .

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DETERMINATION OF FREE CARBON IN BORON CARBIDE - A PROGRESS REPORT

T. D. Tarr

Existing procedures for the determination of free carbon in boron carbide involve the oxidation of the carbon with dichromate-sulfuric acid solutions and measurement of the carbon dioxide produced manometrically or gravimetrically.^{1,2} However, it is known that this technique yields only approximate results at best because the combined carbon also is oxidized to some extent.

In the present work, a new approach based upon the use of an oxygen plasma oxidizer is being studied for the selective oxidation of the free carbon. Oxygen is passed through the plasma reactor containing the boron carbide sample, and the RF field within the reactor converts the molecular oxygen to atomic (excited) oxygen. Hopefully, the atomic oxygen will react with the free carbon at a low temperature, and boron carbide will remain unreacted. The sample weight loss will be equal to the free carbon content. In this report, brief descriptions are given of the approaches by which the study is being made and a few preliminary results are presented.

EXPERIMENTAL

Reagents and Apparatus

Boron Carbide, NBL F1048.

Elemental Boron, Eagle-Picher high-purity (> 99%).

Graphite, pyrolytic.

Sample Dishes, Coors porcelain rectangular dishes, 18 ml (A. H. Thomas No. 6725-H 24). The dishes are heated at 300°C for 1 hr and stored in a desiccator.

Plasma Oxidizer, International Plasma Corporation, Model 1003B, equipped with two 3 in. x 6 in. quartz reaction chambers. A satisfactory vacuum is achieved in the instrument with a 150 l/min oil vacuum pump. Tank oxygen is supplied via a flow meter.

Oxidation Procedure

Remove boric oxide, boric acid and elemental boron from a boron carbide sample by refluxing the sample in 4N HNO₃ for 2 hr. Wash the sample by decantation thoroughly with water and dry it at 110°C for 2 hr. Add 800 to 1000 mg of sample to a tared sample dish, distributing it evenly over the bottom, and weigh the sample to the

nearest 0.1 mg. Place the dish in the apparatus, and adjust the oxygen flow to about 200 ml/min and the chamber pressure to 4 torr. Initiate the plasma with a power output of 240 watts. Oxidize for 30 min, remove the sample, cool in a desiccator for 30 min, and weigh the sample. Mix the sample gently to expose fresh surfaces and oxidize as before. Continue these steps until a maximum weight loss has been achieved, a point indicated by a weight gain relative to the previous weighing. Calculate the total relative loss in weight; this value is equal to the free carbon concentration in the sample.

RESULTS AND DISCUSSION

Operating Conditions. No study was made of the optimum operating conditions of the plasma oxidizer. Instead, the general conditions proposed by Bersin³ and Boyd and Jeffrey⁴ for the fastest oxidation of graphite with the identical apparatus were maintained. With a suggested approximate 1:1 ratio of RF power (watts) to oxygen flow (ml/min), 240 watts and 200 ml of O₂/min were used; this flow rate gave a pressure of 4 to 5 torr.

Sample Pretreatment. Besides free carbon, boron carbide can contain quantities of elemental boron, boric oxide, boric acid and water in addition to the trace elements. Initial attempts to oxidize the free carbon gave inconsistent weight losses presumably because of the presence of some or all of these substances. Although tests with dry elemental boron indicated no significant weight change after 6 hr in the plasma oxidizer, the elemental boron, along with the water, boric oxide and boric acid, was removed from the boron carbide by refluxing in 4N HNO₃ for 2 hr. The carbide was then washed and dried as described in the proposed procedure. Weight losses from this material in the oxidizer were now much more consistent. Probably most of the previous difficulty was due to the water and boric acid content.

Effect of Particle Size. Pretreated boron carbide sample NBL-F1048 was sieved into 5 particle size ranges. Each sieved portion was then oxidized in the plasma apparatus, Table I. The data indicate that the weight loss increases as the particle size decreases. Additional work is necessary to establish whether or not the increased weight loss is due to free carbon segregation in the fines or to the greater ease in oxidizing free or combined carbon with the smaller particle size.

TABLE I
PLASMA OXIDATION OF SIEVED FRACTIONS OF BORON CARBIDE

<u>Fraction, mesh</u>	<u>Weight Loss, %</u>
+ 80	0.84
- 80 + 100	1.46
-100 + 150	2.11
-150 + 200	2.43
-200 + 325	3.03

Total Carbon and Boron Analyses. One method of learning if boron carbide bonds are broken during the plasma oxidation is to determine total carbon and total boron changes. For example, if the total carbon decreases on oxidation, one can say that the weight loss is due to loss of free or combined carbon. If it is combined carbon that is being oxidized and lost, boric oxide is formed, the quantity of which can be determined easily by analyzing for water-soluble boron.

Total carbon determinations were carried out by ignition in an induction furnace and measurement by gas chromatography. Boron analyses were made by the conventional mannitol titration after fusion of the carbide in sodium carbonate to obtain the total boron, or after leaching with dilute acid to obtain the soluble boron (boric oxide or boric acid).

Total carbon results obtained on the sieved fractions before and after oxidation are presented in Table II along with the weight losses shown in Table I. The decrease in total carbon can be seen to be fairly close to the weight loss for each fraction. The precision of the carbon determinations is poor because of the small samples, about 30 mg. Changes have been made in the gas chromatographic measurements to permit larger samples to be used in future work. At any rate, the weight loss in the samples is apparently due to oxidation of free or combined carbon.

TABLE II
ANALYSES OF SIEVED FRACTIONS FOR TOTAL CARBON
BEFORE AND AFTER OXIDATION

Fraction, mesh	Total Carbon, %				Difference, %	Weight Loss, %
	Before Oxidation	RSD, %	After Oxidation	RSD, %		
+ 80	23.35	0.23	22.29	0.09	1.06	0.84
- 80 + 100	22.49	0.29	21.26	0.04	1.23	1.46
-100 + 150	22.48	0.13	20.80	0.19	1.68	2.11
-150 + 200	22.78	0.26	20.70	0.19	2.08	2.43
-200 + 325	22.88	0.05	19.90	0.12	2.98	3.03

One sieved fraction, -200 + 325, was analyzed for soluble boron after the oxidation. Only 0.32% boric oxide was found. In all probability, then, the boron carbide was not seriously attacked by the oxidation; the weight loss was due chiefly to the oxidation of the free carbon. Future work will be carried out in this area.

X-Ray Diffraction Studies. Lipp⁵ has reported that the X-ray diffraction pattern of boron carbide shows a peak due to free carbon (graphite) at a 2θ of 26.6° . In the present work, X-ray diffraction patterns were made of leached and dried carbide before and after plasma oxidation. In several tests the free carbon peak present in the carbide decreased to a small fraction of its initial height and a small broad boric oxide peak not present previously appears. This appearance of boric oxide confirms the boron analysis

work described above. It is believed that the production of this boric oxide is responsible for the weight gain that signals the end of the free carbon oxidation.

To determine the lower limit of detection of free carbon in boron carbide by X-ray diffraction, boron carbide with essentially no free carbon is needed to which one can add quantities of carbon. To obtain such a material, a boron carbide sample was treated with the hot sodium dichromate- H_2SO_4 solution in an attempt to oxidize all the free carbon (plus some carbide carbon). The product was examined by X-ray diffraction for the free carbon peak. After repeated treatment with the oxidizing reagent, free carbon was still present.

In another approach the plasma oxidizer was used to oxidize the free carbon. After 3 hr of oxidation, no free carbon peak could be seen. The material was then leached with dilute acid to remove any boric oxide, and then it was dried. When this material was spiked with pyrolytic graphite and the mixtures analyzed by X-ray diffraction, no consistent results were obtained. When these mixtures were plasma oxidized, the added carbon spikes appeared to burn off in 2 hr. When the material was spiked to 0.2 to 3.0% carbon with pelletized graphite, the X-ray diffraction results now stepped off more consistently.

In another series of tests, boron carbide previously treated by plasma oxidation was spiked with graphite identical to that used in the manufacture of boron carbide. The mixtures were then plasma oxidized for 1 hr, Table III. Also shown in Table III are some boric oxide determinations on the oxidized products.

TABLE III

PLASMA OXIDATION OF SYNTHETIC BLENDS OF BORON CARBIDE AND GRAPHITE

<u>Free Graphite Added, %</u>	<u>Weight Loss by Plasma Oxidation, %</u>	<u>Boric Oxide Leached from Final Product, %</u>	<u>Corrected Weight Loss by Plasma Oxidation (Free Carbon), %</u>
0.94 ^a	1.07	-	-
2.32 ^a	2.35	-	-
7.73 ^b	7.66	1.05	7.57
7.83 ^b	8.27 ^c	1.07	8.18 ^c
5.44 ^b	5.57	1.06	5.48
1.96 ^b	2.12	1.12	2.02

a. -80 + 100 mesh boron carbide

b. unsieved boron carbide

c. a small amount of sample was lost during a weighing.

It can be seen that the corrected weight loss in each case agrees reasonably well with the free graphite added.

ACKNOWLEDGMENT

The author wishes to thank A. J. Busch for the X-ray diffraction analyses.

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PRELIMINARY EVALUATION OF A RAPID MASS SPECTROMETRIC METHOD OF DETERMINING BORON ISOTOPIC ABUNDANCE IN BORON CARBIDE

A. W. Summers

At the New Brunswick Laboratory (NBL), boron carbide is analyzed for isotopic abundance by the mass spectrometer after conversion of the boron carbide to sodium tetraborate.¹ The conversion step involves a sodium carbonate fusion of the sample, a cation-exchange separation of the boron to remove the large quantities of sodium ion and other impurities, and neutralization of the purified boric acid to pH 9.0 to obtain sodium tetraborate. These steps require considerable time and effort, and they open up the possibility of changing the isotopic ratio by contamination and variations in reagent purity.

Recently, direct procedures for analyzing boron carbide have been described in which the conversion to sodium tetraborate takes place on the mass spectrometer filament. For example, Spitzer and Sites² place elemental boron or a boron compound on a tantalum filament containing a small amount of sodium hydroxide and heat the filament to 750°C. Rein and Abernathy³ confirmed the production of the Na_2BO_2^+ spectrum by the method of Spitzer and Sites but found that the ion production was erratic. They propose a similar procedure based on using pulverized boron carbide and sodium hydroxide blended in a 1:1 weight ratio and adding a portion of this blend to the filament for the preparation of the sodium tetraborate. These carefully prepared mixtures were deemed necessary because Shields and co-workers⁴ have reported that the measured $^{11}\text{B}/^{10}\text{B}$ ratios were in part dependent upon the Na/B ratio.

Goheen⁵ simply adds a suspension of about 0.1 mg of boron carbide in roughly 20 μl of 1% sodium carbonate to a tantalum filament previously prepared by adding a portion of the 1% sodium carbonate and heating to a glass-like melt. The filament temperature is finally raised until the fusion reaction occurs.

In the present work, a procedure nearly identical to that of Spitzer and Sites² was evaluated. A portion of a suspension of the boron carbide in sodium hydroxide solution is placed on a tantalum filament, and the temperature is raised until reaction occurs. The charged filament is then analyzed.

EXPERIMENTAL

Reagents and Apparatus

Sodium Hydroxide Solution, 1, 3, 5 and 10%.

Standard Boric Acid. National Bureau of Standards (NBS) SRM No. 952. This boric acid is both an assay and an isotopic standard.

Tuberculin Syringe, 1 ml, equipped with a No. 26 needle. A short length of teflon tubing is slipped over the needle.

Mass Spectrometer, PDP-8 computer controlled, first-order, directional focusing, thermal ionization, with a 6-in. radius and a 60° magnet sector. Canoe-shaped tantalum filaments 0.0012 in. by 0.030 in. are used.

Charge Box, with variac-controlled 6V transformer.

Procedure

Add about 0.5 mg of boron carbide powder to a 5 ml polyethylene vial containing about 100 μ l of sodium hydroxide solution and mix. By means of the syringe and teflon tube, transfer a small quantity of this suspension to a filament in the charge box through which is passing a current of 1.2A. Gradually increase the current until a sudden glow on the filament at about 2.4A indicates that the reaction producing sodium tetraborate has occurred. Place the charged filament in the mass spectrometer and measure the Na_2BO_2^+ ion peaks at masses 88 and 89.

RESULTS AND DISCUSSION

A sample of natural boron carbide obtained from Cerac Incorporated was analyzed by the proposed method, Table I. Since no boron carbide isotopic standards exist, these data were compared to results obtained at the same time with the identical boron carbide converted to sodium tetraborate by the conventional NBL method. The proposed method shows a standard deviation of 0.004 in the $^{11}\text{B}/^{10}\text{B}$ ratio and a positive bias of 0.24% when compared to the standard method.

An enriched boron carbide powder was then analyzed, Table II. Two charges by the proposed method again gave a positive bias of 0.27% when compared to the standard method.

In a final series of analyses, three charges of NBS SRM No. 952 boric acid were analyzed by the proposed method and the results were compared to the certified value, Table III. Again, the proposed method shows a bias of 0.23%.

This bias of 0.23 to 0.27% does not change with the sodium hydroxide concentration of the solution (B/Na ratio), filament current ranges of 1.40 to 1.55A, or filament heating times, the three factors found by Shields and co-workers to influence the $^{11}\text{B}/^{10}\text{B}$ ratio. The precision of the method appears to be as good as the more involved conversion method. The bias of the method appears to be fairly constant and could be included in the correction factor of the mass spectrometer. However, additional work is planned as time permits to discover the reason for the bias.

TABLE I
ANALYSIS OF NATURAL BORON CARBIDE BY PROPOSED PROCEDURE
AND CONVENTIONAL CONVERSION

<u>Number of Charges</u>	<u>Filament Current, A</u>	<u>Filament^a Heating Time, hr</u>	<u>NaOH Solution Concentration, %</u>	<u>¹¹B/¹⁰B^b Ratio</u>
(Proposed Procedure)				
3	1.45, 1.40, 1.50	-	10	4.026, 4.036, 4.028
4	1.40, 1.40, 1.45, 1.35	-	5	4.037, 4.033, 4.032, 4.027
1	1.45	1	5	4.030
1	1.55	2	5	4.032
2	1.55, 1.50	3	5	4.042, 4.036
1	1.40	4	5	4.043
1	1.45	-	3	4.026
1	1.50	2	3	4.034
1	1.45	3	3	4.029
3	1.50, 1.50, 1.55	-	1	4.031, 4.034, 4.028
1	1.50	1	1	4.030

Overall Average = 4.032

Standard Deviation = 0.006

(Conventional Conversion Procedure)

4	1.30, 1.30, 1.25, 1.30	-	-	4.019, 4.022, 4.025, 4.021
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Overall Average = 4.022

Standard Deviation = 0.003

Ratio of Proposed Procedure/Conventional Conversion = $\frac{4.032}{4.022} = 1.025$

a. residence time in mass spectrometer

b. result corresponding to listed filament currents,
respectively.

TABLE II

ANALYSIS OF ENRICHED BORON CARBIDE BY PROPOSED PROCEDURE
AND CONVENTIONAL CONVERSION

<u>Number of Charges</u>	<u>Filament Current, A</u>	<u>Filament Heating Time, hr</u>	<u>NaOH Solution Concentration, %</u>	<u>$^{11}\text{B}/^{10}\text{B}$ Ratio</u>
(Proposed Procedure)				
1	1.5	-	1	0.08611
1	1.6	3	1	0.08623
1	1.6	-	1	0.08617
1	1.6	3	1	0.08624
Overall Average = 0.08619				
(Conventional Conversion Procedure)				
3	1.3	-	-	0.08606, 0.08593, 0.08590
Overall Average = 0.08596				
Ratio of Proposed Procedure/Conventional Conversion = $0.08619 / 0.08596 = 1.0027$				

TABLE III

ANALYSIS OF NBS SRM NO. 952 BY PROPOSED PROCEDURE

<u>Number of Charges</u>	<u>NaOH Solution Concentration, %</u>	<u>$^{11}\text{B}/^{10}\text{B}$ Ratio</u>
3	1	0.05332, 0.05337, 0.05333
Average = 0.05334		

Ratio of Proposed
Procedure/Certified Value = $0.05334 / 0.05319 = 1.0023$

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A CURRENT EVALUATION OF THE ISOTOPE DILUTION MASS SPECTROMETRIC PROCEDURE FOR DETERMINING URANIUM AND PLUTONIUM

P.C.Puleio, C.E.Pietri, A.W.Wenzel, R.J.Greer, G.E.Peoples and
A.W.Summers

At the New Brunswick Laboratory (NBL) the determination of uranium and plutonium in irradiated fuel element dissolver solutions, low level waste, and some scrap materials is carried out by isotope dilution mass spectrometry. This procedure, along with an evaluation of the reliability of the determinations, has been described in detail in a previous report.¹ In the present work, the precision and accuracy of the procedure were re-assessed by the analysis of uranium and plutonium standards under routine operating conditions over an extended period of time.

EXPERIMENTAL

Reagents and Apparatus

Except for the following changes, the reagents and apparatus were the same as previously described:

Uranium Standards. Two solutions, Standard A and Standard B, were prepared from NBL dingot uranium metal, 99.972%. The standards were made to contain about 850 and 740 $\mu\text{g/ml}$, respectively, in dilute HNO_3 .

Plutonium Standard. A solution was prepared from National Bureau of Standards (NBS) SRM No. 948, $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, to contain about 7.5 $\mu\text{g Pu/ml}$.

Mass Spectrometer. The instrument described previously¹ was modified by the installation of a NBL-designed vacuum lock.²

Procedure

The standardization of the ^{233}U and ^{242}Pu tracers and the analysis of the sample solutions are described in reference (1). One exception was the increase from 1×10^{-6} g to 2.5×10^{-6} g plutonium charge for the filament loading. All determinations were made with the first stage collector (Faraday cup), and the plutonium standard-tracer (S-T) mixtures were analyzed separately from the uranium S-T mixtures.

RESULTS AND DISCUSSION

Over a period of four months, 12 Pu S-T mixtures, prepared from the Pu standard solution and the standardized ^{242}Pu tracer, were analyzed. Similarly over a six-week period, 14 U S-T mixtures, prepared from the two U standard solutions and the standardized

^{233}U tracer were analyzed. All of these S-T mixtures were made under actual operating conditions along with the preparation of routine inventory samples. Thus, no special treatment was given the standards. Roughly, 1 S-T standard was prepared for every 5 inventory samples.

The Pu data are shown in Table I. A relative standard deviation (RSD) of 0.20% is indicated, with no bias at the 95% confidence limits (C.L.). The U data, Table II, show a RSD of 0.40% with no bias. These precisions are not statistically different.

TABLE I
ACCURACY AND PRECISION STUDY FOR PLUTONIUM

<u>Pu Added, μg</u>	<u>Pu Found, μg</u>	<u>Relative Difference, %</u>
7.566	7.552	-0.18
"	7.564	-0.03
"	7.581	+0.20
"	7.545	-0.28
"	7.549	-0.22
"	7.589	+0.30
"	7.582	+0.20
"	7.554	-0.15
"	7.583	+0.22
"	7.577	+0.15
"	7.574	+0.11
"	7.580	+0.19
Average Relative Difference, % = +0.042		
Relative Standard Deviation, % = 0.20		

TABLE II
ACCURACY AND PRECISION STUDIES FOR URANIUM

	<u>Uranium Added, μg</u>	<u>Uranium Found, μg</u>	<u>Relative Difference, %</u>
Standard A	0.8533	0.8541	+0.09
	"	0.8553	+0.23
	"	0.8518	-0.18
	"	0.8571	+0.44
	"	0.8573	-0.70
	"	0.8568	+0.41
	"	0.8546	+0.15
	"	0.8520	-0.15
		Average	+0.036
Standard B	0.7445	0.7453	+0.10
	"	0.7435	-0.14
	"	0.7408	-0.50
	"	0.7487	+0.56
	"	0.7400	-0.61
	"	0.7424	-0.28
	"	0.7445	-0.005
	"	0.7477	+0.42
	"	0.7449	+0.05
	"	0.7400	+0.73
		Average	+0.032

Overall Average Relative Difference, % = +0.035

Relative Standard Deviation, % = 0.40

All the data support the previous evaluation¹ of the precision and accuracy of the NBL isotope dilution procedure. The overall precision of the procedure is apparently limited by the mass spectrometer instrumental precision which has been determined to be 0.27% RSD. This value was obtained by 8 separate analyses of 10 ratios each of NBS SRM U-500 which simulates a 1:1 isotope dilution mixture of $^{233}\text{U}/^{235}\text{U}$ or $^{242}\text{Pu}/^{239}\text{Pu}$. The NBS U standard is customarily used for Pu work also since no comparable Pu standard is available.

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AN IMPROVED VACUUM LOCK FOR A THERMAL-IONIZATION SOURCE MASS SPECTROMETER

E.L. Callis, A.W. Summers, V.E. Connolly and P.C. Puleio

In a previous report,¹ a vacuum lock was described for each of two thermal ionization source mass spectrometers used at the New Brunswick Laboratory (NBL) for uranium isotopic abundance determinations. With these vacuum locks, which shortened the sample analysis time by 50%, the entire sample bar with sample attached is removed and placed in a holder when a fresh sample is installed. This operation obviously is not desirable with a radioactive sample. Accordingly, a modified vacuum lock was designed for operation on a tandem instrument used chiefly for the analysis of plutonium and uranium-233.

Design for Radioactive Samples

The design permits all sample handling to be carried out inside an open-front box surrounding the mass-spectrometer source unit and serving to limit the spread of any activity dislodged from the sample filaments. The modification consists of mounting the vacuum lock housing on a hinge so that it may be swung aside to permit access to the sample holder. The hinge is double acting in that it allows a small amount, about 1 in., of movement of the housing along its longitudinal axis in addition to angular displacement. The housing is made of aluminum to reduce the weight supported by the hinge. Originally, the sample insertion bar was also made of aluminum, but because of outgassing problems it was later replaced with a conventional stainless steel bar. The lock is shown in the open position in Figure 1.

Modification to Existing Vacuum Locks

A modification was made to the locks used for the analysis of uranium to improve their operation. This change is an improved electrical contact system which provides a larger contact area and a more positive and reliable connection, Figure 2. This modification was incorporated as a design change in the lock used for plutonium analysis.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Austin Padgett, now retired, who fabricated two of the locks and designed the clever hinge used on the swing-away model.

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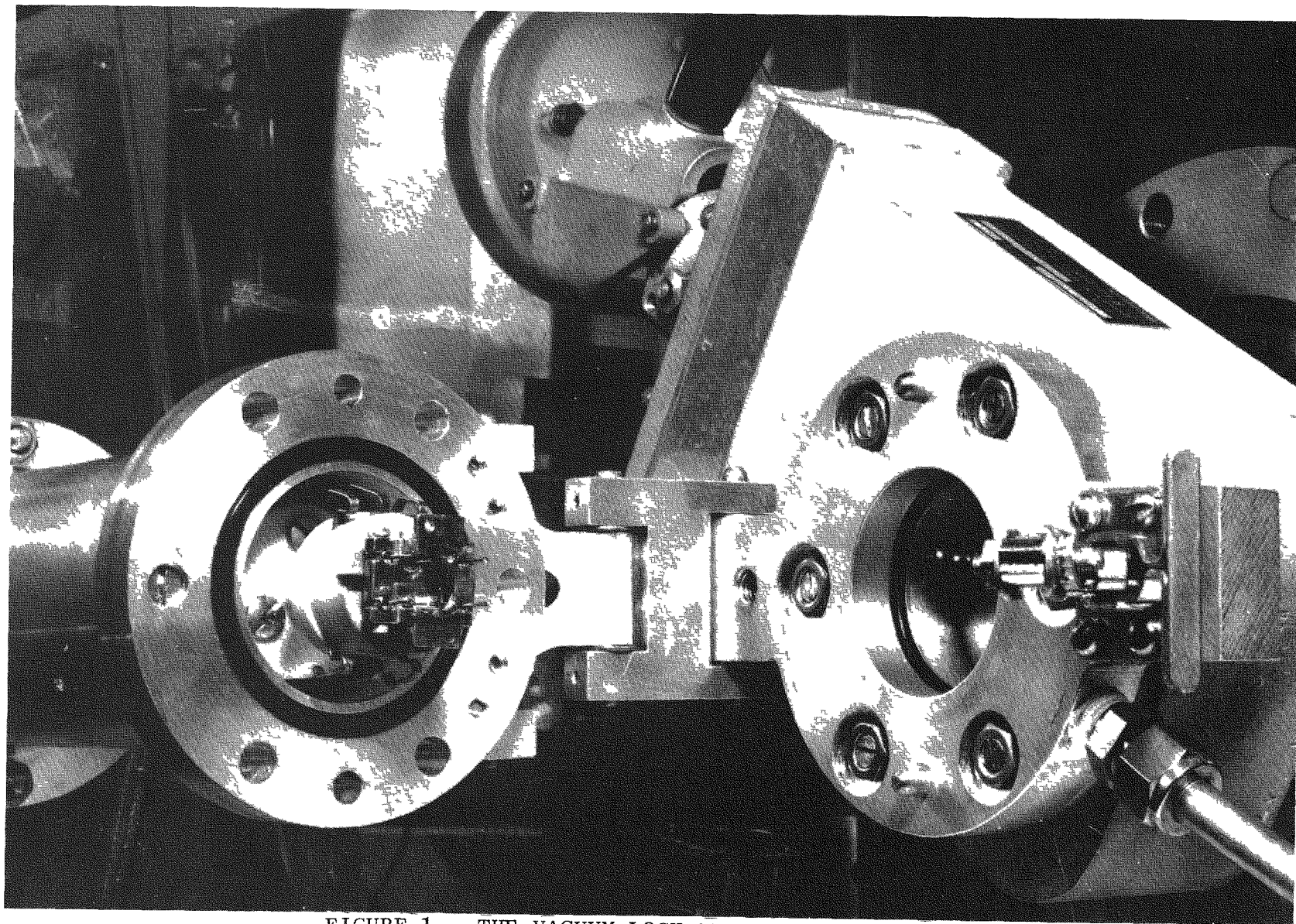


FIGURE 1. THE VACUUM LOCK IN THE OPEN POSITION

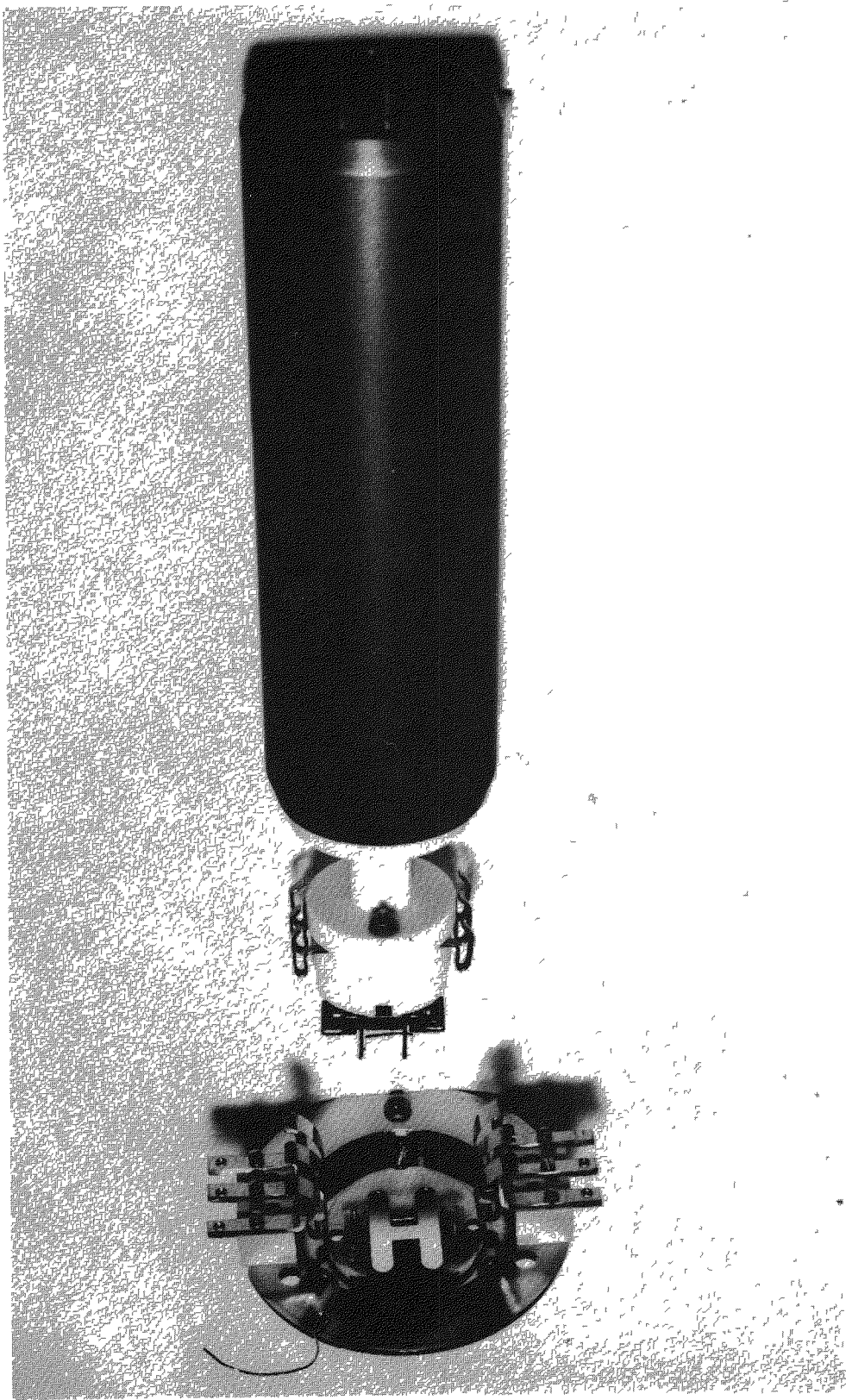


FIGURE 2. DETAILS OF THE IMPROVED ELECTRICAL CONTACTS WHICH SUPPLY POWER TO THE FILAMENTS

PREPARATION OF URANIUM CHARGE MATERIAL FOR MASS SPECTROMETRIC ISOTOPIC ANALYSIS

A. Holub

Because of the increasing number of samples received at the New Brunswick Laboratory (NBL), better methods from the standpoint of reliability and speed are urgently needed for many routine analyses. In the present report, two improved procedures for the separation of uranium from most mixtures including thorium are described. These procedures have been in use now for some months, replacing the previous procedures described by Paller¹ and Siddons.² The purified uranium is dissolved in nitric acid for the charge material in the mass spectrometric analyses.

These modified procedures are somewhat more rapid than those used previously. Furthermore, fewer procedural steps and less handling of the samples decrease the chances of contamination, a primary concern in isotopic analysis.

EXPERIMENTAL

Reagents and Apparatus

Nitric Acid, (1+9) and 0.1N.

Ammonium Nitrate Crystals, reagent-grade.

Ether, reagent-grade.

Hydrochloric Acid, 8M.

Anion-Exchange Resin, Dowex 1-X8, 50-100 mesh.

Ion-Exchange Column, micro-Jones reductor.

Ammonium Hydroxide, freshly prepared by saturating distilled water with tank ammonia.

Procedure (in the absence of thorium)

Transfer a portion of the sample solution containing about 50 to 75 mg of U to a 100-ml beaker. Heat the solution to boiling and add NH_4OH until the solution is strongly ammoniacal. Filter the solution through Whatman No. 40 paper, discarding the filtrate. Dissolve the precipitate in the paper with a total of 30 ml hot (1+9) HNO_3 , collecting the solution in a 4-oz narrow-mouth polyethylene bottle. Saturate the cooled solution with ammonium nitrate.

Add 30 ml of ether, cap the bottle, and shake the mixture for 5 min. Allow the phases to separate, and draw off the ether layer with a disposable pipet into the original beaker now containing about 15 ml of water. Evaporate the mixture to dryness on a steam bath, adding a few drops of HNO_3 when the ether has evaporated. Dissolve the sample in a few milliliters of HNO_3 for the isotopic analysis. If it is suspected that organic matter is present in the final solution, add a few drops of HClO_4 and evaporate the solution to dryness. Take up the residue again in HNO_3 .

Procedure (in the presence of thorium)

Transfer a portion of the sample solution containing about 25 to 50 mg of U to a 250-ml beaker. Heat the solution to boiling, precipitate and collect the U as in the above procedure. Dissolve the precipitate with 100 ml of hot 8M HCl for the ion-exchange separation.

Prepare an anion-exchange column to contain about 6 in. of settled resin and condition the column by passing 25 ml of 8M HCl through it at a flow rate of about 3 ml/min. Add the uranium solution in 8M HCl to the column and elute the uranium with 100 ml 0.1N HNO_3 .

Evaporate the solution to dryness on a steam bath. If the residue does not look like fairly pure uranyl nitrate hexahydrate, carry out an ether extraction as described above, otherwise dissolve it in HNO_3 for the isotopic analysis.

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SPARK-SOURCE MASS SPECTROMETRIC DETERMINATION OF IMPURITIES IN URANIUM HEXAFLUORIDE IN THE GASEOUS PHASE

E. L. Callis

The determination of a broad range of impurities in uranium hexafluoride is usually accomplished by conversion of the hexafluoride to the oxide and subsequent analysis by emission spectrometry.^{1,2} Another instrumental technique involving the "freeze-drying" of hydrolyzed hexafluoride and analysis by spark source mass spectrometry has also been reported.³ Since these conversion processes involve considerable effort and time, and may in some cases result in losses of certain elements, an attempt is being made at the New Brunswick Laboratory to develop a method for the direct determination of impurities by spark source techniques.

EXPERIMENTAL

Instrumentation

The spark source mass spectrograph is an AEI (Associated Electrical Industries, Ltd.) MS-7 instrument modified for electrical detection by the manufacturer. In the present work, the photoplate is used exclusively.

A simple room-temperature inlet system was fabricated. It consists of a sample reservoir and an inlet valve to admit the hexafluoride gas into the source region. Since the inlet system must be connected electrically to the electrodes to prevent a glow discharge in the inlet tube, the entire inlet system is insulated from ground and is "floated" at the accelerating potential of 20 kV.

The hexafluoride gas was ionized by introducing it into a conventional spark discharge between suitable electrodes such as silver or copper through a small longitudinal hole drilled through one of the electrode pair and connecting this electrode to the hexafluoride feed by means of teflon tubing.

RESULTS AND DISCUSSION

The spectrum produced by this technique is, as one might expect, more complicated than a conventional spark source spectrum. The UF_n^+ ions, where n can be 0 to 5, are present at a relative intensity decreasing by about a factor of three for each additional fluoride atom. The ratio of U^+ ions to the electrode material ion is approximately one.

A spark voltage of about 15 kV was found to give the best compromise between excessive production of complex ions and the maintenance of an acceptable total beam intensity. Elements which

have been detected in a variety of UF_6 samples include W, Re, I, Se, As, Ge, Ru, Nb, S, P, Si and B.

A limitation of this simple room-temperature inlet system is that only elements present as compounds with a significant vapor pressure at room temperature can be detected. In addition, the composition of the sample in the reservoir changes as the compounds of higher vapor pressure are depleted.

Accordingly, a new inlet system is being made in which a measured volume of liquid UF_6 can be heated to a maximum of 300°C and the gas allowed to expand into a large reservoir at about 1 atmosphere pressure. From this reservoir, the gas will be leaked into the source region. This procedure should enable the detection of less volatile impurities and, in addition, produce a single-phase sample. Also being built at this time is a source made of nickel and Monel to replace the existing tantalum source which is attacked by UF_6 .

A complete report of this work will be issued at a later date.

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SECONDARY CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF CHROMIUM(VI) WITH IRON AS AN INTERMEDIATE

K. Lewis

The coulometric reduction of chromium(VI) became of interest during an investigation of the reliability of a controlled-potential coulometer and cell system. An iron solution was used initially, but a satisfactory iron standard was difficult to obtain. Primary standard grade potassium dichromate is readily available, and the controlled-potential coulometric reduction of a standard solution prepared from this material appeared to be an ideal test of a coulometric system.

A literature search revealed three references to the coulometric reduction of dichromate. Harrington, Propst, and Britt¹ carried out the reduction at a gold electrode to prepare a chromium(III) solution, and an accuracy of about 1% was considered to be adequate for this purpose. Rechnitz and Srinivasan² studied the reduction by differential controlled-potential coulometry with two cells and compared the results with those obtained by primary controlled-potential coulometry at a platinum electrode. The results by the latter technique were 0.4 to 1.4% low as compared to the theoretical value. Merritt, Martin and Bedi³ obtained precise and accurate results by adding an excess of sodium iodide to the solution so that the electrochemical reduction obtained was that of the iodine formed by reaction of the iodide with the dichromate.

In the present work, it was found that the controlled-potential coulometric reduction of potassium dichromate would not occur readily at a platinum electrode. The reduction would occur at a gold working electrode, but the results were about 0.2% low. A secondary controlled-potential coulometric procedure similar to that of Merritt et al.³ with an iron intermediate was finally utilized and found to be satisfactory.

EXPERIMENTAL

Reagents and Apparatus

Iron Solution, 2 to 5 mg/g solution, prepared from iron wire by dissolution in H_2SO_4 ; final solution is 0.5M in H_2SO_4 .

Potassium Dichromate Solution, 2 to 5 mg/g solution, prepared from primary standard grade $\text{K}_2\text{Cr}_2\text{O}_7$ with the weighings corrected for buoyancy and purity; two solutions were made: solution No. 1 and No. 2.

Coulometer, M-T Model 3 Controlled-Potential Coulometer System.

Cell, 50 mm tall weighing bottle with 40/12 T opening, equipped with a fitted teflon cap with holes for the working electrode, the platinum and calomel electrode, the purge gas inlet, and the sample entry.

Working Electrodes, Pt or Au gauze cylinder, 20 to 25 mm high and 35 mm diameter.

Procedure

Add an aliquot of the iron solution, containing a quantity of iron equal to or greater than the equivalent amount of dichromate to be determined, to the cell and add sufficient 0.5M H_2SO_4 to cover the working platinum electrode. Deaerate the solution by passing an inert gas stream (nitrogen) over the surface for 10 min. Reduce the iron at a potential of +0.19V vs SCE until the current decreases to a low constant value of about 5 μA . Zero the integrator and, with the coulometer still on, add 5 to 10 mg of dichromate; record the time. Allow the reduction to continue to a steady residual current of 5 μA or less, then record the integrator readout vs time. When the change in integrator readout per unit time, ΔQ , is constant, record the final integrated readout and the time. Multiply ΔQ by the total time and subtract this product from the final integrated readout to obtain the integrated readout corrected for the continuous background current. Calculate the quantity of potassium dichromate by using this value in Faraday's Law.

RESULTS AND DISCUSSION

Attempts to reduce potassium dichromate coulometrically at a platinum electrode failed: the initial currents were very low indicating that the electrode reaction was very sluggish. The use of a gold working electrode led to a considerable improvement with high initial currents and reasonable reduction times being obtained. The results were reproducible, but with solution No. 1 a negative bias of 0.2% was found. A further check on another solution of dichromate, solution No. 2, again gave precise but negatively biased results. The actual recovery of dichromate for the two solutions was 99.83% and 99.75%, respectively. Thus, these data confirm the experience of Rechnitz and Srinivasan² who obtained negative errors using this direct technique.

The indirect determination of the dichromate by a secondary controlled-potential coulometric procedure with iron(II) as the electrochemically active intermediate was then attempted. The chemical reaction between iron(II) and dichromate is known to be fast and stoichiometric. Therefore, it should be possible to reduce an iron solution to the iron(II) state, add a quantity of dichromate to form an equivalent amount of iron(III), and then to coulometrically reduce the iron(III) produced.

Initial results obtained by reducing the iron solution, turning off the coulometer, and adding the dichromate solution were not very reproducible and were invariably high. It appeared that a portion of the ferrous ion was oxidized when the coulometer was off. Improved results were obtained when the coulometer was left on after the iron reduction and during the dichromate addition, Table I.

TABLE I
COMPARATIVE RESULTS WITH DIFFERENT TECHNIQUES

<u>K₂Cr₂O₇ Solution</u>	<u>No. of Runs</u>		<u>Relative Standard Deviation, %</u>	<u>Recovery, %</u>
	<u>Direct Technique</u>	<u>Indirect (Secondary) Technique</u>		
1	8		0.03	99.83
2	4		0.03	99.75
1		5	0.03	100.00
2		2	(agree to 0.05)	99.90
2		3	0.16	100.32
		(coulometer off during sample addition)		

The recovery of the dichromate by the secondary coulometric technique can be seen to be 99.90 to 100.00%. This difference between solutions of 0.10% is essentially the same as that found by the direct procedure. Solution No. 2, on which the lower recovery was obtained, was an old solution prepared some months previously, and the strong possibility exists that some reduction of the dichromate occurred on opening the container many times during storage. This phenomenon has been observed in a previous study.⁴

On the basis of these results, it can be stated that the secondary coulometric procedure is useful for confirming the prepared value of a potassium dichromate solution. Possibly ceric or permanganate solutions can be tested in the same manner.

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THE EFFECT OF RESIDUAL OXYGEN AND ELECTRODE TREATMENT ON THE CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF IRON

K. Lewis

Previous controlled-potential coulometric work¹ on plutonium and iron solutions carried out by the author with platinum electrodes indicated that the electrode condition and the presence of residual amounts of oxygen seriously affected the electrolytic reduction behavior. Reductions in some cases became unreasonably slow; the time taken to attain acceptable background currents led to long titration times and uncertainty in the completeness of the reduction. A further investigation of these effects has now been carried out and is reported here.

EXPERIMENTAL

Reagents and Apparatus

Iron Solution, 2-5 mg per g of solution, prepared from pure iron metal by dissolution in nitric acid.

Coulometer, M-T Model 3 Controlled-Potential Coulometer System.

Cell, 50 mm tall weighing bottle with a 40/12 T mouth, fitted with a teflon stopper containing openings for the working, auxiliary and reference electrodes, a gas inlet, and the sample introduction. The solution volume needed to cover the working electrode is 30 ml.

Electrode, Pt gauze cylinder, 20 to 25 mm high and 35 mm o.d.

Procedure

Coulometry. Carry out the controlled-potential coulometric determination of the iron in the solution, previously purged of oxygen, either by reduction alone at +0.19V vs SCE or by reduction at this potential followed by oxidation at +0.68V vs SCE. In either case, time the titration and follow the electrolysis until the current decays to a low, constant value. At this point, measure the change in integrated readout per unit time, ΔQ , until the value becomes constant, then stop the titration and record the final integrated readout, ΔQ , and the time. Multiply ΔQ by the titration time and subtract the product from the final readout to obtain the integrated readout corrected for the continuous background current. Determine a blank in the same manner. Calculate the quantity of iron titrated from the corrected readout by means of Faraday's Law.

Treatment of Electrode. Immerse the electrode in boiling HNO_3 for 5 min. Rinse thoroughly in distilled water.

RESULTS AND DISCUSSION

Initial coulometric determinations were carried out by placing the iron solution in the cell, adding electrolyte solution to cover

the working electrode, deaerating by passing a nitrogen stream over the solution surface for 10 min, and then electrolyzing. It was observed in both the iron and blank measurement that the initial reduction behavior was variable. At times the reduction readouts were high and the decrease in current to background levels was slow. At other times, the readout values were more reasonable and the current decay to low background levels occurred more readily. It was also noted that particularly troublesome reduction behavior was experienced after the electrode was treated to obtain higher initial currents. This behavior was observed also in the blank determinations; therefore, it was clearly not related to the iron solution but was due either to the reduction of a constituent in the electrolyte or to an electrode surface effect. Since it was suspected that this behavior was caused by residual oxygen, an examination was made of various means of eliminating oxygen more completely from the solution.

Two methods of deaeration were studied, and they were evaluated by comparing data obtained for the reduction of a ferric solution. The first method consisted of nearly filling the cell with electrolyte solution, sparging vigorously for 10 min with nitrogen at a flow rate of 500 to 600 ml/min, raising the gas inlet to maintain a nitrogen atmosphere in the cell, prereducing the solution, then adding the ferric solution and reducing the ferric ion.

The second method differed only in that the gas inlet was not raised; a continuous sparge was maintained but the flow rate was decreased to 100 to 200 ml/min to avoid spray losses. The results are shown in Table I.

TABLE I
REDUCTION OF FERRIC ION WITH TWO METHODS OF DEAERATION

<u>Deaeration Method</u>		<u>No. of Runs</u>	<u>Fe(III) Recovery, %</u>	<u>Relative Standard Deviation, %</u>
No. 1	Sparge changed to N ₂ overflow	8	100.19	0.08
No. 2	Continuous sparge	8	99.96	0.06

The difference in the results shown in Table I is undoubtedly due to the presence of oxygen in the ferric solution. This oxygen is apparently not removed when the cell solution itself is not sparged after the addition of the iron solution (Method No. 1). Thus the effect of residual oxygen can be seen to be quite significant. More data were then accumulated by the continuous sparge technique (No. 2) and an average recovery of 99.99% with a relative standard deviation of 0.04% was obtained with a total of 39 runs.

A confirmation of the above conclusion was obtained by sparging the electrolyte solution, raising the gas inlet, adding an iron(III) sample and then coulometrically reducing and oxidizing the iron, Table II.

TABLE II
COMPARISON OF COULOMETRIC REDUCTION AND OXIDATION WITH
DEAERATION BY METHOD NO. 1

<u>Coulometric Titration</u>	<u>No. of Runs</u>	<u>Iron Recovery, %</u>	<u>Relative Standard Deviation, %</u>
Reduction	5	100.30	0.11
Oxidation	5	99.97	0.03

From the data in Tables II and I, it can be seen that the recovery by coulometric oxidation which is not affected by the presence of oxygen is essentially the same as that obtained by reduction when the residual oxygen is removed by a continuous sparge. The high results due to traces of oxygen are again shown by the reduction data in Table II.

Effect of Electrode Treatment. As noted above, the reduction behavior with the gas overflow deaeration technique was particularly troublesome after cleaning the electrode with HNO_3 : very high blank runs with slow current decays were observed. This effect was apparently due to an increase in the electro-chemical activity of the electrode resulting from the acid treatment. The reduction of not only the iron occurred at a faster rate but also the oxygen and impurities. The elimination of the excessively high blanks by the use of the more efficient sparging clearly indicates that oxygen was the primary reducible species causing the difficulty.

An additional effect observed with freshly treated electrodes, of a slower rate of current decay to background levels even in well deaerated solutions, was found to be due to the increased sensitivity of the electrode to traces of impurities accumulated in stored electrolyte solutions. The use of freshly prepared or pretreated electrolyte solutions eliminated this difficulty.

One more point should be mentioned. The effectiveness of deaeration by the gas overflow method appears to depend on the solution volume and other factors. For example, a solution volume of 30 ml with a nitrogen flow rate of about 500 ml/min was used in the work reported here, and the oxygen removal was not complete. However, in a recent report by Harrar,² in which deaeration by gas overflow was recommended, only a 15-ml volume and a very high flow rate, at least 2 l/min, were used. Harrar also noted that complete oxygen removal depended on the absence of air bubbles trapped in the gauze electrode or between the electrode and cell walls when the cell is filled.

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SEPARATION OF ANTIMONY FROM URANIUM BY COLLECTION ON MANGANESE DIOXIDE — AN EVALUATION

C. E. Hedrick

The need exists for a reliable chemical method of determining antimony, ideally in the 0.01- to 10-ppm range, in uranium product materials. Numerous instrumental methods are available that are helpful for low levels of antimony. For example, an emission spectrographic procedure involving carrier distillation from a gallium oxide matrix^{1,2} has been described. An atomic absorption spectrophotometric measurement after extraction of the antimony with an organic solvent has been reported.³ Spark source mass spectrography has determined lower-ppm quantities of antimony in uranium.^{4,5}

Chemical methods require a preliminary separation of the antimony. These separations, summarized by Sandell,⁶ include coprecipitation on copper sulfide⁷ and manganese dioxide.^{8,9} Solvent extraction from an iodide medium has been used for quantitative separation.¹⁰ Reduction to stibine and collection in mercuric chloride or potassium permanganate solution is another standard procedure.¹¹ In the present work the separation by collection on manganese dioxide was evaluated for the analysis of uranium. The isolated antimony was measured spectrophotometrically in the ultraviolet as the antimony-iodide complex because of its simplicity and sensitivity.¹²

EXPERIMENTAL

Reagents and Apparatus

Iodide-Ascorbic Acid Reagent. Dissolve 112 g potassium iodide and 20 g ascorbic acid in 500 ml of water, filter and dilute to 1 l. Prepare fresh daily.

Antimony Standard Solution, 10 $\mu\text{g/ml}$. Dissolve 0.5986 g antimony trioxide in 25 ml of 50% H_2SO_4 , heating the acid to complete the dissolution. Dilute to 125 ml with 25% H_2SO_4 , cool, and dilute to 250 ml with 25% H_2SO_4 in a volumetric flask. Dilute 0.5 ml of this solution to 100 ml in a volumetric flask with 25% H_2SO_4 .

Centrifuge, International Model BE57, equipped with heads for 50-ml centrifuge tubes and 250-ml plastic bottles.

Spectrophotometer, Beckman Model DU with 10-cm Corex cells.

Procedure

Separation. Dissolve 10 g uranyl nitrate in about 200 ml of 1.2N HNO_3 . Add 5 ml 5% manganese sulfate solution, heat the mixed

solution to boiling and filter it if it is cloudy. To the hot solution add with stirring 3 ml of 1.25% potassium permanganate. Allow the solution to stand to coagulate the MnO_2 . Transfer the solution to a 250-ml plastic centrifuge bottle and centrifuge for 3 min at a rheostat setting of 50. Allow the head to stop without braking, and then decant the supernatant to less than 30 ml. Suspend the residue in the remaining liquid and transfer to a 50-ml conical centrifuge tube. Centrifuge as before and discard the supernatant. Wash the MnO_2 twice with 35 ml of boiling water, centrifuging after each wash. After the final washing, centrifuging and decanting, add 10 ml 2N H_2SO_4 , heat the mixture nearly to boiling and dissolve the MnO_2 by adding 30% hydrogen peroxide dropwise. Destroy the excess peroxide by adding 1.25% potassium permanganate solution dropwise until a faint permanent precipitate appears.

Add 5 ml of the 1.25% potassium permanganate solution and allow the precipitate to coagulate. Centrifuge, decant the supernatant liquid and wash twice with boiling water as before. Add to the residue from the final decanting 5 ml of H_2O and 2 ml of H_2SO_4 . Dissolve the MnO_2 by adding 30% hydrogen peroxide dropwise. Cool the solution, add 2 ml of H_2SO_4 and add the permanganate solution until a faint pink color persists. Cool the solution and transfer it to a 50-ml volumetric flask, using only a small amount of wash water so that the final volume is < 25 ml.

Measurement. Pipet 25.00 ml of iodide-ascorbic acid reagent into the flask, cool the contents to room temperature (25°C) and make up to volume with water. Measure the absorbance in 10-cm cells at 330 nm against a reference prepared by adding 25.00 ml of the iodide-ascorbic acid reagent to 4 ml of H_2SO_4 and 15 ml of H_2O in a 50-ml volumetric flask and diluting to volume with H_2O . Determine a reagent blank by carrying 200 ml of 1.2N nitric acid through the procedure. Subtract the blank absorbance from the sample absorbance.

Prepare a calibration curve by carrying through the procedure 0, 1, 3, 5, 10, 15 and 20 μg of antimony in 200 ml of 1.2N HNO_3 and measuring the absorbance of each solution against the 0- μg solution.

RESULTS AND DISCUSSION

The absorbance values obtained by taking varying quantities of antimony through the entire procedure for the preparation of the standard curve are shown in Table I. Also shown in Table I are the absorbance values obtained by developing the color in the appropriate way with the color-producing reagents and similar quantities of antimony. As shown by the values in the 4th and 5th columns, there is a definite loss in antimony by the MnO_2 carrier technique. This loss amounts to approximately 45% of the initial antimony.

Uranium interferes in the spectrophotometry of the antimony iodide complex. Initial experiments carried out with and without uranium being present during the collection of antimony with MnO_2 indicated that the uranium was removed efficiently.

TABLE I
SPECTROPHOTOMETRIC MEASUREMENTS OF ANTIMONY

Sb, μg	Absorbance Values, A		Average Sb Loss	
	Direct	Through Procedure	μg	%
1	0.055		-	-
2	0.086	0.051, 0.027	1.1	55
5	0.203	0.116, 0.128	2.4	48
10	0.409	0.237, 0.240	4.2	42
15	0.603	0.354, 0.366	6.1	41
20	0.802	0.455, 0.451	8.8	44

Bismuth, thallium, tin and gold also form iodide complexes that absorb strongly in the ultra-violet. Sandell¹³ states that these elements are removed by the carrying of antimony on MnO_2 at acidities of about 1N. Tests were made with 100 μg of bismuth carried through the procedure along with 16.5 μg of antimony. Large amounts of the bismuth survived the separation and seriously interfered with the subsequent spectrophotometric measurements.

From these results it can be concluded that despite the statements in the literature the separation of antimony by coprecipitation with MnO_2 is a poor technique for the determination of antimony for the following reasons:

1. only about 45% recovery is obtained;
2. the recovery is not strictly reproducible;
3. interfering bismuth is not removed by separation.

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ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF IMPURITIES IN ELEMENTAL BORON

R. L. Graff

Impurities in elemental boron were determined by atomic absorption spectrophotometry after dissolution of the sample by treatment with nitric and sulfuric acid, and volatilization of the boron as the methyl ester. The removal of the boron made possible the necessary low dilution of highly-pure material so that the desired sensitivity for many impurity elements could be reached.

EXPERIMENTAL

Reagents and Apparatus

Sulfuric and Nitric Acid, and Methyl Alcohol, redistilled from quartz.

Impurity Standard Solutions, 1 mg/ml, prepared from high-purity materials and made up in 10% by volume H_2SO_4 and 1% by volume HNO_3 .

Atomic Absorption Spectrophotometer, Perkin-Elmer Model 403, equipped with air-acetylene and nitrous oxide-acetylene burner heads together with the necessary hollow cathode lamps.

Procedure

Sample Preparation. To a 1-g sample in a 130-ml platinum dish add HNO_3 carefully in small portions until the rapid reaction subsides, then add 25 ml HNO_3 and apply low heat until there is little further reaction. Add 35 ml of H_2SO_4 and, with more heat, evaporate the mixture to fumes. Carefully add HNO_3 dropwise to the fuming solution until the sample is completely in solution and about 5 to 8 ml of the H_2SO_4 is fumed off. Cool the solution and add with stirring 25 ml of methyl alcohol.

Maintain the solution at medium heat for 1 to 2 hr to volatilize methyl borate. Increase the heat until fuming occurs and again add HNO_3 dropwise until the solution clears. Cool the solution and carry out two more methyl alcohol additions, with 15 ml and 10 ml, and the subsequent evaporations and fuming with HNO_3 additions. At the end of the last fuming, when about 5 ml of H_2SO_4 remains, dilute the solution to the required volume, generally 50 ml, to give an equivalent sample concentration of 2 g/100 ml.

Analysis. Obtain the atomic absorption spectrophotometric measurements following the general procedures given in the Perkin-Elmer manual. Use the 10X absorbance and the 100-average readout mode. Compare the sample absorbance with the standard curve of absorbance versus concentration prepared from the impurity standards.

RESULTS AND DISCUSSION

Dilution of the final solution to 50 ml after sample dissolution and removal of the boron gives an equivalent sample concentration of 2 g/100 ml which is satisfactory for most samples, from fairly impure boron to high purity or ultra-high purity material. Although higher sample concentrations, e.g. from 2 to 10 g/100 ml, would be more desirable from the standpoint of measurement since they give more stable readings, this concentration of 2 g/100 ml is generally used for two reasons: it becomes increasingly difficult to dissolve completely more than a 1-g sample; smaller final volumes decrease the number of determinations that can be made. In Table I, in which the impurity levels found for an ultra-high purity boron are given along with the equivalent sample concentration of solution used, it can be seen that the 2 g/100 ml concentration is apparently satisfactory for all the elements listed.

Fusion dissolution is much faster than acid dissolution but there is a considerable matrix effect and higher blanks in the final atomic absorption measurements. Some brief tests were made with fusion dissolution: 0.3 g sample plus 6 g potassium carbonate. Acidifying the solution of the melt with HNO_3 gives a more stable solution and one that atomizes better than the normal alkaline solution. However, boric acid solubility now prevents sample concentrations much above 0.5 g/100 ml. Such dilute solutions are satisfactory for impure boron samples and give results indistinguishable from the acid preparations. The silicon results by fusion are also shown in Table I. It is of interest to note that the silicon atomic absorption values from acid dissolution and fusion agree well.

For impure samples containing very high levels of chromium, iron and nickel, it was found necessary to dilute all preparations to 0.05 g/100 ml. At this concentration, matrix effects from either fusion or acid dissolution do not exist and instrumental readings are generally in the optimum readout range of the instrument.

Two standard purity and one ultra-high purity boron were analyzed by both atomic absorption spectrophotometry and by emission spectrography, Table II. Both methods at times have given poor agreement with duplicate preparations. In some cases at least, the lack of agreement was traced to inhomogeneity of the samples. At any rate, the ultra-high purity preparation was divided into two portions for the two types of measurements to eliminate this factor.

The data in Table II indicate that acid dissolution-atomic

TABLE I

EFFECT OF EQUIVALENT SAMPLE CONCENTRATION ON ATOMIC ABSORPTION SPECTROPHOTOMETRIC
RESULTS WITH ULTRA-HIGH PURITY BORON

NBL-F4078

Equivalent Sample
Concentration,
g/100 ml

Element Concentration, ppm

	<u>Al</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Na</u>	<u>K</u>	<u>Si</u>
10 g B	10.5	1.5	6.5	4.5	6.6	2.0	0.6	1.9	
	11.0	1.1	6.6	5.0	6.8	3.3		1.9	
	10.5	1.0	6.6	4.0		2.3		2.0	
				5.0		2.1			
						2.3			
5 g B	15.0	1.0	5.0	7.4	1.0	2.0	0.5	1.5	
	5.0			8.0					
				7.0					
2 g B	7.5	1.5	7.0	4.0	2.0	2.7	1.5	2.5	350.0
	10.0		7.5	4.0	2.5	2.8		3.0	350.0
	11.5			5.0	3.0				
				4.5					
1 g B	10.0	1.0	7.5	a	a	a	1.5	a	
	25.0	2.0	7.0						
0.3 g B	a	a	a	a	a	a	a	a	370.0

a. reliable reading could not be obtained.

TABLE II

COMPARISON OF ATOMIC ABSORPTION SPECTROPHOTOMETRIC AND EMISSION SPECTROGRAPHIC VALUES

NBL Sample No.	Method	Element Concentration, ppm					
		<u>Al</u>	<u>Ca</u>	<u>Cu</u>	<u>Cr</u>	<u>Fe</u>	<u>Mg</u>
F4078	AA ^a	7.5	5.0	6	0.8	7.5	3.0
	ES ^b	6-8	6.3	7-9	0.5-0.8	5-7	1.5-4
F4359	AA	-	-	1.3%	5000-5300	3200-4000	112-130
	ES	50-130	-	1.3%	3800-6700	3700-5400	140
F4360	AA	40-60	-	1.0%	2400-2700	1020-1400	470-520
	ES	50	-	1.0%	1900	1600	450
		<u>Mn</u>	<u>Ni</u>	<u>Na</u>	<u>K</u>	<u>Si</u>	
F4078	AA	0.2	2.2	1.5	4.0	370	
	ES	0.1	0.5-1.5	5.0	2.0	250	
F4359	AA	-	2.0%	4-14	20-30	1950	
	ES	-	2.5%	-	-	-	
F4360	AA	-	1.6%	-	65	1300	
	ES	-	2.0%	-	-	-	

a. atomic absorption

b. emission spectrography

absorption spectrophotometry gives results that in most cases agree fairly well with those obtained by acid dissolution-emission spectrometry. One difference does exist, however, which cannot be ascribed to inhomogeneity and that is the higher value for silicon given by atomic absorption. This same method bias for silicon has been found in previous studies.¹

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EVALUATION OF A DEUTERIUM-ARC BACKGROUND CORRECTOR FOR THE ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF IMPURITIES IN URANIUM SOLUTION — A PROGRESS REPORT

R. L. Graff

An evaluation of the Perkin-Elmer Deuterium Arc Background Corrector¹ recently acquired by the New Brunswick Laboratory (NBL) was made by analyzing uranium solutions with and without the Corrector and comparing the results for certain impurities with those obtained by emission spectrography. This method of background correction is reported to be highly efficient², although increased instability at high scale expansion may nullify its benefits.

It was found that the Corrector improved the results of some impurities at the trace levels and had little effect on others. The evaluation will be continued in future work.

EXPERIMENTAL

Reagents and Apparatus

Standards. Solutions of uranium containing 2% and 10% uranium and 5% by volume HNO₃ were prepared from uranyl nitrate hexahydrate assuming a 52% uranium content, and certain impurities were added in desired concentrations. Additional standards used were the NBL-95 series spectrographic standards and the NBL 95-7 blank material.

Atomic Absorption Spectrophotometer, Perkin-Elmer No. 403, equipped with associated hollow cathode lamps.

Deuterium Arc Background Corrector, Perkin-Elmer No. 303-0295, installed in the spectrophotometer and equipped with a phasing switch.

Procedure

Obtain the atomic absorption spectrophotometer measurements with the nitrous oxide-acetylene flame for aluminum and chromium, and the air-acetylene flame for copper, iron, manganese, chromium and nickel. Follow the instrumental manual for the details of the measurements.

RESULTS AND DISCUSSION

Standard curves were prepared from both sets of standards: those prepared for the present work for the 6 elements under investigation, and the NBL series 95 emission spectrographic

standards. Two samples of uranyl nitrate hexahydrate, the July 1972 General Analytical Evaluation (GAE) samples, were then analyzed with and without the Background Corrector, Table I. Both samples were prepared at the 2% and 10% uranium concentration levels for the measurements.

TABLE I

COMPARISON OF ATOMIC ABSORPTION SPECTROPHOTOMETRIC RESULTS
WITH AND WITHOUT THE USE OF THE BACKGROUND CORRECTOR WITH
EMISSION SPECTROGRAPHIC RESULTS

Element	E.S. ^a	GAE No. 1		ppm	GAE No. 2	
		A.A. ^b Without Corrector	A.A. ^b With Corrector		A.A. ^b Without Corrector	A.A. ^b With Corrector
Al	3	6	2.4 ^c	4	7	4.4 ^c
Cr	9	5,6 ^c	5 ^{c,d}	17	14,12 ^c	12 ^{c,d}
Cu	1	1.3	0.8	1	1.3	0.9
Fe	25	20	26 ^c	40	35	41 ^c
Mn	3	1	2 ^c	2	1	2 ^c
Ni	3	7	4 ^c	7	9	6 ^c

a. emission spectrography

b. atomic absorption spectrophotometry

c. 10% U concentration; all others 2% U

d. with air-acetylene flame.

From Table I it can be seen that the atomic absorption spectrophotometric values agreed better with the emission spectrographic values when the Background Corrector was used in the case of aluminum, iron, manganese and nickel. With the limited data obtained, the copper data revealed no clear-cut effect, although the standard curves for copper for 10% uranium concentration, Figure 1, show that the Corrector improved the standard curve by eliminating the matrix absorption. This same effect, less pronounced, appears also in the curves for nickel, manganese, aluminum and iron.

The Corrector did not improve the results for chromium. The exact reason for this failure is unknown at present. Perhaps the nitrous oxide-acetylene flame used for the chromium may not be suitable for the Corrector. Also, the deuterium output is starting to fall off at the chromium wavelength, and balancing the two beams is difficult. The Corrector appeared to be more satisfactory for most elements at the 10% uranium concentration level than at the 2% level.

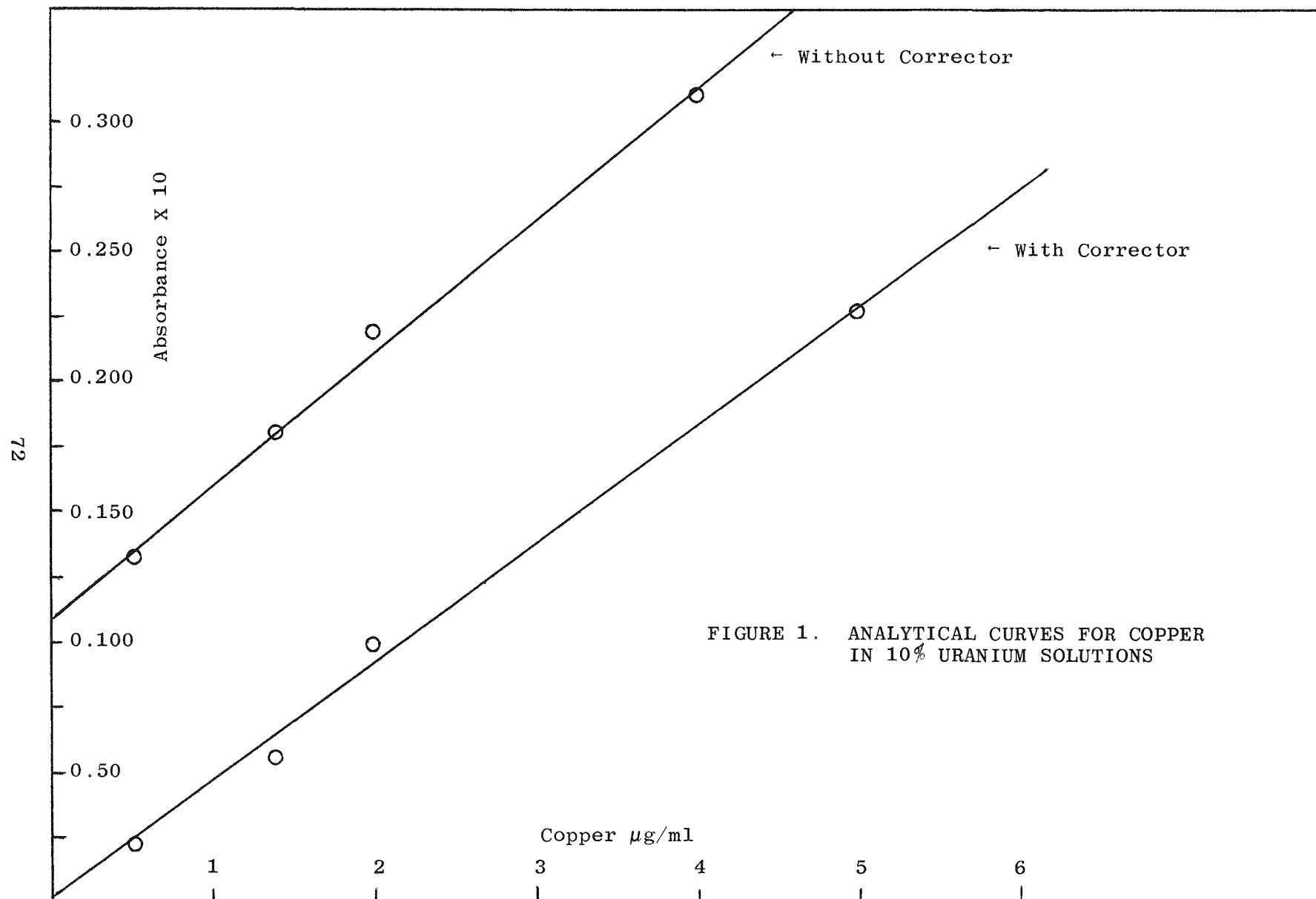


FIGURE 1. ANALYTICAL CURVES FOR COPPER
IN 10% URANIUM SOLUTIONS

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DETERMINATION OF URANIUM-235 ISOTOPIC ABUNDANCE WITH THE INTERFERENCE SPECTROMETER — A PROGRESS REPORT

H. G. Yuster

This report describes the studies made to date on the determination of the isotopic abundance of uranium-235 by the Fabry-Perot interference spectrometer known by the trade-name Hypeac. The interference spectrometer has been used in the past for the isotopic analysis of uranium. Brody, Tomkins and Fred¹ examined uranium isotopic lines with an instrument of their design and construction, and they were able to analyze uranium isotopically when the uranium-235 was at least 4%. The Hypeac was used by Artaud, Gerstenkorn and Blaise² in the study of the 5027 Å uranium line. The separation of the uranium-235 and uranium-238 lines is about 0.1 Å, but the line is intense with hollow cathode excitation and shows almost negligible hyperfine structure of the odd number isotope uranium-235. Bertholet and Lauer³⁻⁵ studied the uranium line at 5027 Å with the Hypeac and a peak integrator. Difficulty was experienced in maintaining a constant baseline with the automatic integrator. In the analysis of National Bureau of Standards (NBS) uranium isotopic standard U-200, the uranium-236 in 0.21% concentration was separated. However, the uranium-234 in 0.13% concentration was not separated from the uranium-235 in 20% concentration. In later work^{6,7} a digital voltmeter and printer measured both peak length and baseline.

In the present work, the uranium line at 5027 Å was also used because the etalon plates supplied with the instrument had fixed quartz spacers of about 3.7 mm, a value based upon calculation involving the wave number interval between orders for the resolved 5027 Å lines. This wavelength is advantageous for the present work also because the monochromator grating is blazed for 5000 Å in the second order and, accordingly, the sensitivity for the 5027 Å region will be optimum.³ A series of samples previously analyzed by the mass spectrometer were studied. The uranium-235 concentrations of these samples ranged from normal to about 10%. The data from these samples were used to develop an empirical equation for the calculation of the uranium-235 abundance by computer operation.

EXPERIMENTAL

Reagents and Apparatus

Neon, research-grade 99.999% pure, Matheson Gas Products, East Rutherford, N. J.

Indium, 2-mm diameter wire, 99.99% pure, Indium Corporation of America, Utica, N. Y.

Aluminum, 1.25 in. rod, alloy No. 2024, Whitehead Metals, Inc., Carteret, N. J.

Uranyl Nitrate Hexahydrate, production grade.

Nitrogen, liquid.

Fabry-Perot Interference Spectrometer, "Hypeac," manufactured by Jobin-Yvon and Associates, Paris, France, described in detail in references (3) and (8).

Measuring System Modification, photomultiplier high voltage supply, model No. 240A, and high-speed picoammeter, model No. 417, both from Keithley Instruments, Inc., Cleveland, Ohio; strip-chart recorder, model No. 7100B and input module, model No. 17501A, both from Hewlett-Packard, San Diego, California.

Hollow Cathodes, fabricated from aluminum No. 2024 stock. The dimensions were taken from the hollow cathode supplied with the instrument. A modification of the indium wire groove for gasket sealing was made according to the suggestion of Gerstenkorn.⁹

Procedure

Sample Preparation. Weigh 50 mg of uranium nitrate into the cavity of the cathode. Place the cathode on a hot plate at medium heat until a melt is obtained, then tilt the cathode with a pair of tongs until the wall of the cavity is coated to present a maximum of sample surface that will produce a large excitation signal. Increase the hot plate heat until the formation of UO_3 is complete. Cool and install the cathode in the Hypeac with the indium wire as gasket material.

Instrumental Conditions for Analysis

Hollow Cathode: neon pressure - 1 mm Hg
current - 60 to 100 mA
temperature - liquid nitrogen

Photomultiplier: voltage - 500 to 700V
temperature - liquid nitrogen

Picoammeter Current: 1×10^{-8} to 3×10^{-9} A for ^{238}U
 3×10^{-10} to 3×10^{-11} A for ^{235}U

Recorder Setting: preamplifier set for 2V full scale

Time Constant: variable with 3 sec maximum

Scanning Speed: isotopes are pressure scanned with air leak at 1 to 1.5 turns - about 0.4 mm/sec pressure change in F-P chamber

Total Scan: 3 orders

NOTE: Ranges are given for the hollow cathode current and the photomultiplier voltages because adjustments are necessary to measure the ^{238}U peak near full scale of the pen recorder.

RESULTS AND DISCUSSION

Development of Equation to Calculate ^{235}U Abundance

At constant resolution the true peak height ratio can be expressed as follows:

$$R_T = (P_5 - C P_8) / (P_8 - D P_5) \quad (1)$$

where: R_T = true peak height ratio of $^{235}\text{U}/^{238}\text{U}$,
 C = factor to correct for contribution of ^{238}U peak to ^{235}U peak,
 D = factor to correct for contribution of ^{235}U peak to ^{238}U peak,
 P_5 = peak height of ^{235}U , measured,
 P_8 = peak height of ^{238}U , measured.

At low ^{235}U enrichments levels, the $(D P_5)$ term approaches zero;

$$\text{therefore:} \quad R_T = \frac{P_5 - C P_8}{P_8} = \frac{P_5}{P_8} - C \quad (2)$$

$$\text{or} \quad R_T = R_m - C$$

$$\text{or} \quad C = R_m - R_T$$

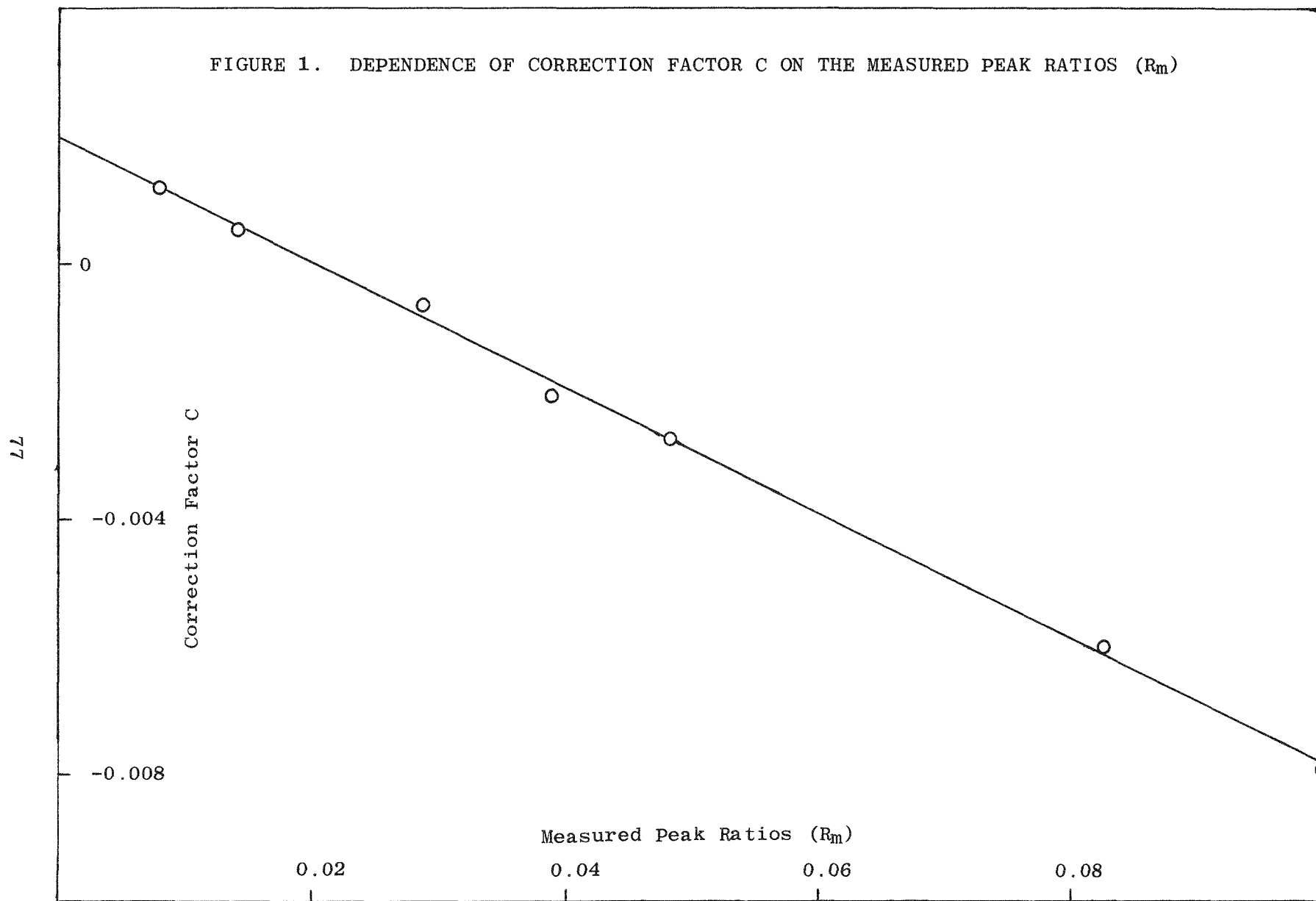
where: R_m = measured peak height ratios.

Table 1 shows the data obtained by measuring the peak height ratios, R_m , of a group of samples on which the R_T values can be calculated from mass spectrometric ^{235}U abundance values by ignoring the ^{234}U and ^{236}U content. In the last column are the correction factor C values calculated from equation (2). A plot of C vs R_m as shown in Figure 1 is a straight line with a slope of -0.098 and an intercept of 0.002.

TABLE I
DETERMINATION OF CORRECTION FACTOR C AT
VARIOUS ^{235}U ENRICHMENTS

<u>NBL Sample No.</u>	<u>R_m</u>	<u>R_T</u>	<u>C</u>
Normal	0.00837	0.00717	+0.00120
EU-16241	0.01427	0.01371	+0.00056
EU-17324	0.02875	0.02939	-0.00064
EU-16676	0.03886	0.04094	-0.00208
EU-17413	0.04822	0.05095	-0.00273
EU-17576	0.08272	0.08873	-0.00601
EU-16635	0.10030	0.10825	-0.00795

FIGURE 1. DEPENDENCE OF CORRECTION FACTOR C ON THE MEASURED PEAK RATIOS (R_m)



The equation for the curve in Figure 1 is

$$C = -0.098 R_m + 0.002 \quad (3)$$

Therefore, substituting the value of C in equation (3) for C in equation (2), one obtains:

$$R_T = 1.098 R_m - 0.002 \quad (4)$$

Now, the isotopic abundance of ^{235}U can be expressed as

$$\begin{aligned} ^{235}\text{U, wt.}\% &= 100 [P_{235}/(P_{235} + P_{238})] \\ &= 100 \left[\frac{P_{235}}{P_{238}} / \left(\frac{P_{235}}{P_{238}} + 1 \right) \right] \end{aligned} \quad (5)$$

where: P is the peak height of ^{235}U or ^{238}U .

$$\text{Therefore, } ^{235}\text{U, wt.}\% = 100 R_T / (R_T + 1) \quad (6)$$

Substituting for R_T its value in equation (4), one obtains:

$$\begin{aligned} ^{235}\text{U, wt.}\% &= 100 (1.098 R_m - 0.002) / (1 + 1.098 R_m - 0.002) \\ &= (109.8 R_m - 0.2) / (1.098 R_m + 0.998) \end{aligned} \quad (7)$$

Equation (7) was used to prepare a computer program in FOCAL language for a Digital Equipment Corporation PDP-15 computer. The program and a printout of a ^{235}U determination as normal uranium are shown in Figure 2.

Data obtained for other ^{235}U enrichments are given in Table II together with estimates of the precision. The relative standard deviation of the determination appears to improve and reach a plateau as the enrichment increases from normal to about 10%. For these data, the recorder tracings were measured with a millimeter scale graduated to 0.5 mm and separate baselines were taken for both the ^{235}U and ^{238}U peaks.

It should be noted that instrumental bias is included in the correction factor determined. Also, since equation (7) is based upon standards containing ^{234}U and ^{236}U , the analysis of samples with approximately the same ^{234}U and ^{236}U content obviously would be more reliable. The ^{234}U , ^{235}U , and ^{236}U abundance of each standard used is shown in Table III. (The ^{238}U abundance can be determined by difference.)

It can be seen that with the exception of sample EU-16676, the contribution of the ^{234}U and ^{236}U to the ^{235}U is fairly constant for the enrichment range covered. Thus, in the analyses of samples of the same origin as the particular standards used, the error should not be too great.

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C FOCAL15 V6A

01.02 A " NOTE: TYPE CTRL/P AFTER LAST SAMPLE ",!!!
 01.03 A "SAMPLE NO. P SUB 235 P SUB 238 % 235 ",!!!
 01.04 A SAM
 01.05 T " "
 01.06 A P35
 01.07 T " "
 01.08 A P38
 01.09 T " "
 01.10 S $WU35 = (109.8 * P35 / P38 - 0.2) / (1.098 * P35 / P38 + 0.998)$
 01.13 T % 6.06, WU35,!
 01.14 GOTO 1.04

*GO

NOTE: TYPE CTRL/P AFTER LAST SAMPLE

SAMPLE NO.	P SUB 235	P SUB 238	% 235
:NORMAL U	:108.0	:13000	0.70715
:	:110.0	:13150	0.71335
:	:110.0	:13150	0.71335
:	:112.0	:13800	0.68639
:	:115.5	:13900	0.70733
:	:113.5	:13550	0.71458
:	:123.5	:14870	0.70689
:	:122.0	:14950	0.69122
:	:126.0	:14750	0.73255
:	:128.0	:14750	0.74722
:	:122.0	:14550	0.71550
:	:122.5	:14400	0.72871
:/P			
FOCAL15 V6A			
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FIGURE 2. COMPUTER PROGRAM AND CONCENTRATION
 READOUT FOR NORMAL URANIUM

TABLE II
PRECISION OF MEASUREMENTS OF ^{235}U ABUNDANCE

NBL Sample No.	^{235}U , wt. %		Number of Determi- nations, N	Standard Deviation, %	Relative Standard Deviation, %
	Mass Spec.	Hypeac			
(Normal)	0.7110	0.7137	12	0.020	2.8
EU-16241	1.352	1.353	12	0.037	2.7
EU-17324	2.855	2.872	12	0.030	0.94
EU-16676	3.933	3.908	12	0.032	0.82
EU-17413	4.848	4.848	12	0.045	0.93
EU-17576	8.150	8.158	12	0.075	0.92
EU-16635	9.768	9.758	12	0.130	1.33

TABLE III
ISOTOPIC ABUNDANCE OF STANDARDS DETERMINED BY
MASS SPECTROMETER

NBL Sample No.	^{234}U	^{235}U	^{236}U	Contribution to
				^{235}U of ^{234}U and ^{236}U , %
(Normal)	0.0055	0.7110	-	0.77
EU-16241	0.0065	1.352	0.0116	1.34
EU-17324	0.0187	2.855	0.0174	0.26
EU-16676	0.0352	3.933	0.0242	1.51
EU-17413	0.0237	4.848	0.0377	1.27
EU-17576	0.0490	8.150	0.0536	1.26
EU-16635	0.0538	9.768	0.0670	1.24

ACKNOWLEDGMENT

The author wishes to express his appreciation to E. L. Callis for his helpful suggestions during phases of the work.

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COBALT AS A SPECTROCHEMICAL INTERNAL STANDARD

R.L. Graff, H.G. Yuster and L.C. Nelson, Jr.

The use of cobalt as a spectrochemical internal standard for gallium oxide-carrier distillation methods is well documented. It is considered to be a reliable internal standard, especially for those elements of moderate volatility: iron, chromium, manganese, nickel and others. However, for some time now it has been observed at the New Brunswick Laboratory (NBL) that, with uranium and thorium oxide standards, the intensity of the cobalt spectral line decreases with an increase in total impurity concentration. Obviously this behavior would indicate that the cobalt is an efficient internal standard only for those samples and standards with about the same quantities of total impurities.

In the present work, the use of cobalt was studied by means of a radioactive tracer technique. Tracer techniques have been used by various investigators to study the volatilization of indium¹ and iron.² The technique has also been relied upon by Vainstein and co-workers in their work on the spatial distribution of various elements in the arc plasma,³ and in their studies on the effect of controlled atmospheres on the spatial distribution.⁴ The techniques are also described in references (5,6).

EXPERIMENTAL

Reagents and Apparatus

Cobalt Chloride, reagent-grade.

Cobalt-60, 1 μ g, as cobalt chloride.

Thorium Oxide Impurity Standards, NBL No. 66 series.

Gallium Oxide, at least 99.998% pure.

Spectrograph, Jarrel-Ash 3.4 m Ebert, with two cylindrical lenses in the external optics, 15000 lines/in. grating, 5.07 Å/mm dispersion, set for 2200 to 4600 Å.

Densitometer, Jarrel-Ash microphotometer.

Calculating Board, Applied Research Laboratories.

Electrodes, upper, ASTM C-1; lower, NC SP9066 (high precision ASTM S-2).

Procedure

Preparation of Carrier-Internal Standard Mixture. Dissolve 538 mg gallium oxide (equivalent to 400 mg gallium metal) in 10 ml of HCl in a platinum dish. Add 5.4 mg cobalt (22 mg cobalt chloride hexahydrate) so that the cobalt is 1% of the gallium oxide weight. Add the radioactive ^{60}Co together with 5 ml of H_2SO_4 and evaporate the solution to dryness on a hot plate. Ignite the residue at 900°C for 2 hr in a furnace. Thoroughly mix and grind in an agate mortar.

Analysis of Standards. Mix 980 mg of each level of the NBL Thorium Oxide Impurity Standard No. 66 series with 20 mg (2% by weight of standard) of the carrier-internal standard mixture, and blend by grinding in an agate mortar.

Weigh 100 mg of each mixture into a lower electrode. Place the electrode in a 3 x 1/2 in. plastic vial and count the gamma activity for 10 min in a scintillation spectrometer. Remove the electrode and analyze the charge under the conditions given below. After burning the sample, place the lower electrode in the same vial and count again.

Exposure Conditions:

Excitation: 14 A shorted; 220V dc
Electrode Gap: 4 mm
Slit: 25 μ wide, 9.1 mm high
Sector: 7 steps rotating
Step Ratio: $I_0/I = 2$
Plate: 4 x 10 in. Eastman Kodak
Spectrum Analysis No. 1
Processing: D-19, 3 min;
Short stop, 30 sec;
Kodak Rapid Fixer, 2 min;
Wash, 2 min.

RESULTS AND DISCUSSION

The data obtained by gamma-counting the ^{60}Co activity before and after the arcing of the charges are shown in Table I. Each number represents an average of 5 runs on each standard and 3 counts on each run.

TABLE I

COBALT-60 ACTIVITY LOSS ON BURNING STANDARDS

Thorium Oxide Standard No.	Before Arcing, cpm	After Arcing, cpm	⁶⁰ Co Volatilized, %
NBL-66-1	406,587	390,812	3.9
66-2	409,977	392,726	4.2
66-3	405,298	386,268	4.7
66-4	406,031	382,155	5.9
66-5	402,656	379,031	5.9
66-6	394,642	370,457	6.1

In Table II are given the results obtained by densitometry of the ⁶⁰Co line at 3044.00 Å. The data of Tables I and II are plotted in Figure 1. Examination of the comparative data reveals that the spectrochemical response curve follows closely the curve for the relative amount of cobalt emitted from the sample. It is evident that high concentrations of impurities do actually decrease the volatilization of the cobalt rather than simply shift the spatial distribution of the cobalt with a corresponding failure to sample the arc plasma efficiently with the external lens system. It is also apparent that a plateau of response occurs from 100 to 400 ppm total impurities. This plateau corresponds to a cobalt loss or volatilization of about 6%, a value close to that found for iron by Atwell and Pepper.²

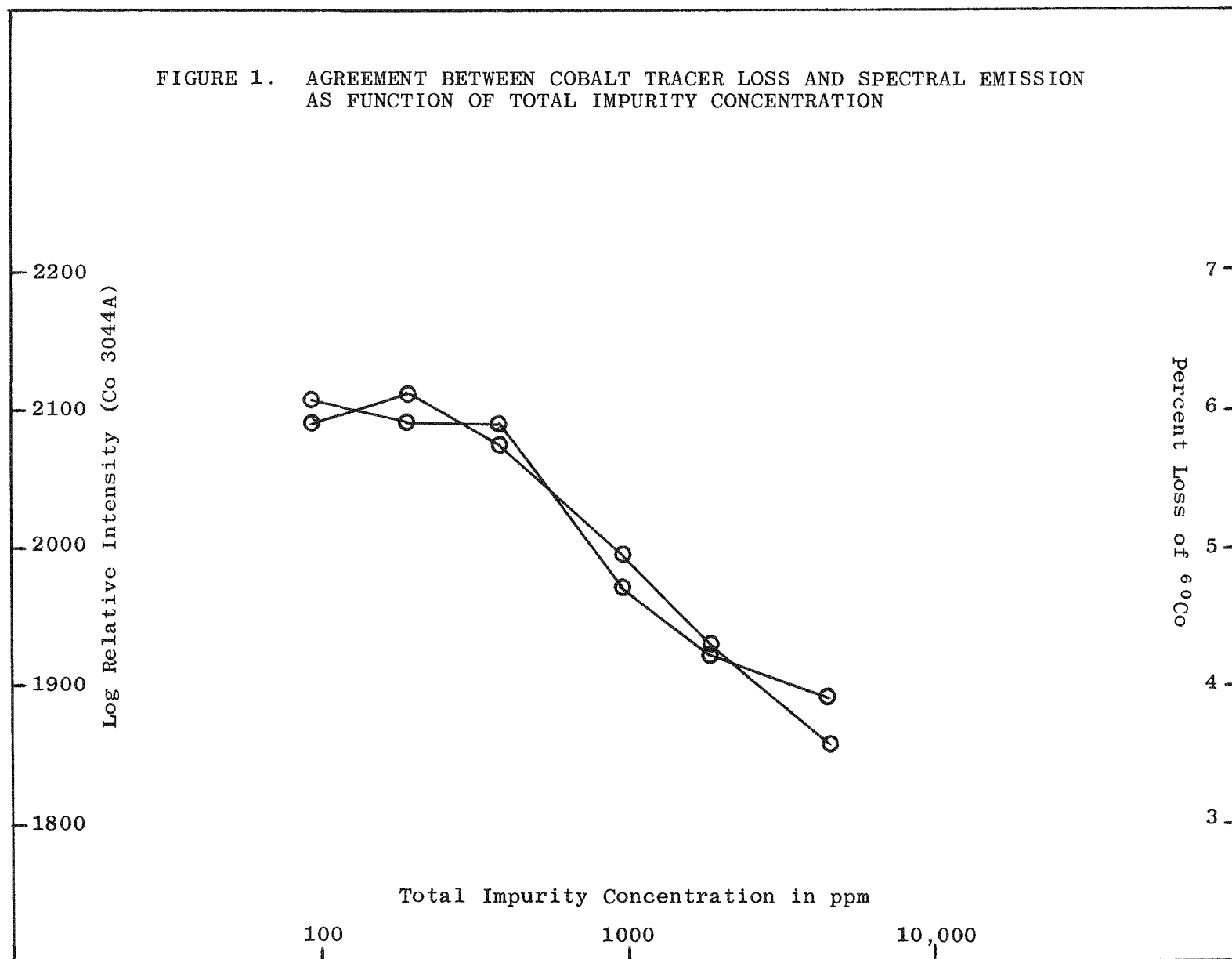
TABLE II

DENSITY OF COBALT LINE AT 3044 Å

Thorium Oxide Standard No.	Total Impurities in Standard, ppm	Log Relative Intensity
NBL-66-1	4600	1.865
66-2	2900	1.930
66-3	950	1.990
66-4	390	2.075
66-5	195	2.110
66-6	95	2.090

It was of interest at this point to compare a select group of elements with a wide range of volatility on the basis of analytical curves prepared with and without the use of the cobalt internal standard. In Table III, in which the data are summarized, the elements that give good analytical curves with each technique are indicated. It can be seen that the cobalt internal standard helps the analysis of silicon, iron and nickel in that more linear curves are obtained, especially at the high concentration end. Only the analysis of the highly volatile boron is not helped by the internal standard technique. Accordingly, the use of the cobalt internal standard technique is recommended for more reliable impurity

FIGURE 1. AGREEMENT BETWEEN COBALT TRACER LOSS AND SPECTRAL EMISSION
AS FUNCTION OF TOTAL IMPURITY CONCENTRATION



analysis despite the fact that the cobalt actually is less volatilized with an increase in total impurity concentration.

TABLE III
EVALUATION OF COBALT AS AN INTERNAL STANDARD

Element (x)	Technique ^a		Element Wavelength, Å
	I_x (Direct)	I_x/I_{Co} (Internal Standard)	
B	+		2497
Si		+	2506
Fe		+	2599
Mn	+	+	2605
Pb	+	+	2833
Ni		+	3050
Cu	+	+	3274
Zn	+	+	3345

a. + = satisfactory analytical curve

The results indicate that silicon, iron and nickel also are less volatile with an increase in the total impurity concentration. Qualitative visual observations appear to confirm this conclusion. It is planned to study these effects on elements other than cobalt in future work as time permits.

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DETERMINATION OF PLUTONIUM AND URANIUM IN PLUTONIUM DIOXIDE-URANIUM DIOXIDE-DYLENE MIXTURES

N.M. Trahey, G.E. Peoples, A.W. Wenzel and C.E. Pietri

Samples of PuO_2 - UO_2 -Dylene were submitted to this laboratory for analysis. This material was made by blending the mixed oxides with 60 mesh Dylene (polystyrene) and hot pressing the mixture into cubes.¹ Shavings of these cubes constituted the analytical samples. Prior to the analysis of the actual samples, preliminary analyses were made of simulated material prepared from PuO_2 , U_3O_8 and Dylene. These exploratory studies are reported here.

EXPERIMENTAL

Reagents and Apparatus

National Bureau of Standards SRM U_3O_8 950a.

Plutonium Dioxide, No. 251, a secondary standard, characterized to be 87.06% Pu.

Dylene, Sinclair-Koppers Co., Monaca, Pa., 60 mesh.

Procedure

Place a suitable weight of mixture in a 50-ml Vycor crucible. Place the crucible in a cold furnace and raise the temperature slowly to 300°C. Maintain at this temperature for 6 to 10 hr, then raise the temperature to 550°C for 3 hr. Cool. Dissolve the oxide residue in dilute HNO_3 for the analyses by the NBL titrimetric methods for uranium² and plutonium.³

RESULTS AND DISCUSSION

In the initial work, a solvent was sought for Dylene to convert the polymer into a physical form somewhat more representative of the actual form in samples. The results of this study are given in Table I. Trichloroethylene (TCE) showed the best solvent characteristics and safety features.⁴ Accordingly, it was used throughout this work.

TABLE I
SOLUBILITY OF DYLENE IN SELECTED ORGANIC SOLVENTS

<u>Amount of Dylene Taken, mg</u>	<u>Solvent</u>	<u>Solvent Volume, ml</u>	<u>Remarks</u>
100	methanol	10	insoluble
100	carbon disulfide	10	dissolves within 15 min
100	chloroform	10	forms a gelatinous mass, then dissolves within 2 hr
100	trichloroethylene	10	dissolves within 3 min
100	ethyl acetate	10	dissolves within 1 hr
100	acetone	10	forms a gelatinous mass, then dissolves in 1 to 2 hr
100	ethanol	10	insoluble
100	1:1 acetone-TCE	20	dissolves in 0.5 to 1 hr
550	2:1 acetone-TCE	30	dissolves in 20 min

A series of mixtures was prepared from U_3O_8 and Dylene with a polymer: oxide ratio of 5. This ratio was selected as being the maximum found in actual samples. These mixtures were analyzed for uranium, Table II. Also analyzed were similar mixtures of Dylene and oxide in Vycor crucibles to which TCE was added and allowed to stand several days until the solvent evaporated and left a Dylene-oxide cake. Analyses of the U_3O_8 used in these mixtures are included in Table II for comparison. The data in Table II show no statistically significant differences. The presence of Dylene, then, does not adversely affect the recovery and determination of uranium.

TABLE II
URANIUM RECOVERY FROM U_3O_8 -DYLENE MIXTURE

<u>Sample</u>	<u>N</u>	<u>Uranium Determination, %</u>	<u>RSD, ^a %</u>
U_3O_8	7	84.730	0.059
U_3O_8 -Dylene, dry	8	84.734	0.074
U_3O_8 -Dylene, TCE	8	84.721	0.086

a. relative standard deviation

In Table III are given the data obtained by analyzing 15% PuO_2 -35% U_3O_8 -50% Dylene mixtures together with the comparative analyses of the U_3O_8 and PuO_2 . Again, no significant effect of the Dylene on the uranium or plutonium determination can be seen. The reproducibilities of the determinations, however, were poor with RSD values larger than generally accepted. Time did not permit a detailed study of the cause of the poor precisions.

TABLE III

URANIUM AND PLUTONIUM RECOVERY FOR PuO_2 - U_3O_8 -DYLENE MIXTURES

<u>Sample</u>	<u>N</u>	<u>U Determination</u>		<u>Pu Determination</u>	
		<u>U, %</u>	<u>RSD, ^a%</u>	<u>Pu, %</u>	<u>RSD, ^a%</u>
U_3O_8	3	84.717	0.003		
U_3O_8 - PuO_2 -Dylene	7	84.733	0.239		
PuO_2	3			87.099	0.481
PuO_2 - U_3O_8 -Dylene	4			87.045	0.211

a. relative standard deviation

These data indicate that PuO_2 - UO_2 -Dylene mixtures presumably can be analyzed by the proposed methods. One factor that may be important in the sample analyses is the potential inhomogeneity of the samples. Observations made here of the U_3O_8 -Dylene cake formed with TCE showed that a uniform cube may be difficult to obtain with a pressing technique which converts the Dylene to a fluid state in which the oxide particles tend to settle rapidly.

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ADJUSTMENT OF PLUTONIUM OXIDATION STATE BY FERROUS AND DICHROMATE ION TREATMENT — A PRELIMINARY STUDY

J.L. Minns, A.W. Wenzel, C.E. Hedrick and C.E. Pietri

A separation of plutonium from impurities by anion exchange in 8M nitric acid¹ is required prior to the determination of plutonium by the New Brunswick Laboratory (NBL) constant current potentiometric titration method.² A critical step in the ion-exchange separation is the quantitative conversion to the plutonium-(IV) oxidation state by treatment of the sample with hydrogen peroxide and moderate heating. In pure solution or in the absence of gross amounts of impurities, the color changes corresponding to the plutonium oxidation states can be utilized. For example, the hydrogen peroxide treatment produces a blue color indicating Pu(III). After standing or gentle heating, the olive-green color of Pu(IV) appears. However, in the presence of large amounts of colored ions such as uranium, these distinctive colors are masked, and some degree of experience is required to detect the proper colors.

Because of this uncertainty, a study is being made of an alternative method of preparing the plutonium(IV) oxidation state. In the proposed method, ferrous ion is used to reduce the plutonium-(VI,IV) to plutonium(III), and potassium dichromate then is used to oxidize the excess ferrous ion and the plutonium(III) to plutonium-(IV). These changes can be detected both amperometrically and potentiometrically. After adjustment to the plutonium(IV) oxidation state, the ion-exchange separation is applied, and the plutonium is determined by titration.

EXPERIMENTAL

Reagents and Apparatus

Ferrous Sulfate, 0.5N — Sulfamic Acid, 1N.

Potassium Dichromate, 0.3N in 1N H₂SO₄.

Sulfamic Acid.

Plutonium Standard Solution, 0.19283 g Pu/g solution, in 8M HNO₃, containing from 0.1 to 1% plutonium(VI) as determined by ion-exchange studies.

Amperometric Apparatus, consisting of a Keithley Model 410A picoammeter, a 1.5V dry cell, a voltage divider with 4.3 and 2.7K ohm resistors, and a platinum and calomel (SCE) electrode pair. In use, a voltage of about 0.9V is applied to the electrodes with the platinum electrode being positive.

Magnetic Stirrer and teflon-coated stirring bar.

pH Meter, with platinum and calomel (SCE) electrodes.

Procedure

Amperometric Detection. In a glove box, transfer sufficient Pu standard solution with $8N$ HNO_3 to contain about 200 mg of Pu to a teflon beaker, add about 0.1 g sulfamic acid, insert the platinum and calomel electrodes of the amperometric apparatus, and begin stirring the solution magnetically. Add the ferrous solution dropwise until a constant current of $3 \mu A$ is obtained. Next, add the dichromate solution dropwise until the current drops to zero, then add a few drops more. Separate the Pu by the anion exchange procedure, and titrate the Pu as previously described.^{1,2}

Potentiometric Detection. Generate Pu(VI) by the following steps: transfer the solution containing 200 mg of Pu to teflon beakers; evaporate the solution to near dryness; take up in $1M$ HNO_3 ; evaporate to near dryness once more and finally dilute to 50 ml with $1M$ HNO_3 . Insert the platinum and calomel electrodes, and stir the solution magnetically. Observe the potential which should read about 540 mV. Add the ferrous solution until the solution reaches a potential of 350 mV. Observe that at this point the color changes from yellow brown to blue. Add a slight excess of ferrous solution until no further change of potential occurs. Add dichromate solution dropwise until the potential increases to about 550 mV, then again add 2 to 3 drops in excess. Note that the color is now olive green. Adjust the acidity from $1M$ HNO_3 to $8M$ by adding HNO_3 ; note that the potential changes from 550 to 660 mV. Separate the Pu by the anion exchange procedure and determine the Pu.

RESULTS AND DISCUSSION

The two end-point detection techniques used appear to be equal in ease of application and of locating the reaction end points. The potentiometric apparatus is, of course, somewhat more easily assembled.

The general procedure appears to work satisfactorily when the Pu(VI) content is low, up to about 1%, as the data in Table I show. However, when the Pu(VI) content is much higher, in excess of 50% as is obtained by prior evaporation of the solution twice with $1M$ HNO_3 and dilution in $8M$ HNO_3 , the losses of Pu in the column separation are as high as 5%.

TABLE I

AMPEROMETRIC DETECTION OF THE Pu(IV) OXIDATION
STATE IN 8N HNO₃

<u>Sample</u>	<u>Plutonium Added, mg</u>	<u>Plutonium Found, mg</u>	<u>Relative Difference, %</u>
S-42-93 ^a	197.73	197.7	+0.02
S-42-99 ^a	195.81	196.1	+0.14
S-42-96 ^a	199.88	200.2	+0.17
S-42-101 ^a	194.23	194.3	+0.02
S-42-43 ^b	194.29	192.7	-0.8
S-42-79 ^b	186.69	182.7	-2.0
S-42-58 ^b	194.54	184.3	-5.3
S-42-38 ^b	207.01	205.7	-0.62

a. Pu(IV) plus < 1% Pu(VI) before adjustment

b. Pu(VI) content at least 50% before adjustment

In the potentiometric detection studies, high concentrations of Pu(VI) were generated in all of the sample solutions as described above.

With these high concentrations of Pu(VI) in 1M HNO₃, Table II, the losses are somewhat lower than shown by the same concentrations in 8M HNO₃ (Table I). Apparently, then, both high acid and Pu(VI) concentrations create a difficult condition for the correct oxidation state adjustment by the proposed procedure. The reduction of Pu(VI) by ferrous ion is relatively slow at either high or low acidity.³ Perhaps insufficient time was allowed for complete reduction in these studies.

In connection with a study on mini-columns for the ion-exchange separation, with 5 mg samples of Pu treated to obtain large concentrations of Pu(VI), the oxidation state adjustment by the proposed method was completely successful.⁵ In these tests the Pu was in 1M HNO₃ prior to the adjustment with the ferrous-dichromate ions.

Additional work will be carried out to investigate the effects of Pu and acid concentrations.

TABLE II
POTENTIOMETRIC DETECTION OF Pu(IV) OXIDATION
STATE IN 1N HNO₃

<u>Sample</u>	<u>Plutonium Added, mg</u>	<u>Plutonium Found, mg</u>	<u>Relative Difference, %</u>
S-52-37	220.35	220.4	+0.01
S-52-24	207.13	206.4	-0.40
S-52-25	187.78	187.7	-0.04
S-52-32	201.69	199.7	-0.98
S-52-22	218.22	215.9	-1.07
S-52-35	209.40	207.2	-1.05
S-52-23	203.77	202.0	-0.85
S-42-44	195.58	195.4	-0.11
S-42-50	199.33	197.1	-1.11

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CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF PLUTONIUM AFTER ION-EXCHANGE SEPARATION IN MINI-COLUMNS

J.R. Weiss, C.E. Pietri, A.W. Wenzel and L.C. Nelson, Jr.

Plutonium is determined routinely at the New Brunswick Laboratory (NBL) by a constant-current potentiometric titration¹ following an ion-exchange separation² of the many elements that interfere in the titration. The method is extremely reliable but it is slow. Accordingly, controlled-potential coulometry was investigated. This method characteristically uses small samples and is adversely affected by few elements.

Unfortunately, many plutonium-bearing samples received at NBL for analysis consist of scrap materials of unknown composition. These samples are not readily analyzed directly by coulometry because of their high salt and impurity content. Moreover, they frequently contain substances such as organic matter that rapidly poison the coulometer electrodes. These samples can only be analyzed by controlled-potential coulometry if the interferences are separated prior to analysis. In the present work, the standard ion-exchange procedure for 100 to 300 mg of plutonium was scaled down to accommodate 5-mg samples. A method currently under study³ for the adjustment of the oxidation state prior to the ion-exchange separation was used for the mini-column separation.

EXPERIMENTAL

Reagents and Apparatus

Ferrous Solution, 0.1N, prepared from iron(II) sulfate heptahydrate.

Potassium Dichromate, 0.07N, prepared from reagent-grade material.

Resin, Dowex 1-X2, 100 to 200 mesh, nitrate form.

Stripping Solution, 0.36M HCl, 0.01M HF.

Sulfamic Acid Solution, saturated.

Plutonium Standards. Standard A. A 20 mg/g solution was prepared from high-purity plutonium metal, 99.95%, by dissolving in 6M HCl, converting to the nitrate by evaporation with HNO₃, and diluting to volume with 8M HNO₃. The concentration was established by careful analyses by the constant-current potentiometric method.

Standard B. A 5 mg/g solution was prepared similarly from National Bureau of Standards SRM 949c plutonium metal.

Argon, 99.996% pure, dry.

Coulometer, M-T Electronics, Model 3.

Cells and Electrodes. The cells are 50-ml lipless beakers with fitted teflon cap and rubber O-ring similar to the type described by Rodden.⁴ A magnetic stirrer with teflon-coated stirring bar is used. Vycor frits on glass tubes are used for the salt bridges. The reference electrode is a saturated calomel electrode (SCE). The counter electrode is a 16-gage platinum wire in the shape of a helix. The working electrode is a cylinder made of expanded gold sheet with a gold support rod.

pH Meter, with platinum and calomel (SCE) electrodes.

Digital Voltmeter, 10-V range, capable of measuring 0.0001V.

Resin Columns. Bio-Rad disposable polypropylene columns No. 7311110, 0.7 cm i.d. The column is filled to a depth of 5 to 6 cm with the resin, and the resin is conditioned with 15 ml of 8M HNO_3 .

Procedure

Sample Preparation. Transfer from 1 to 10 mg of Pu in solution to a 50-ml glass beaker. Add 2 drops of H_2SO_4 and fume to dryness carefully with a heat lamp. Cover the beaker and allow it to cool.

Oxidation State Adjustment. Dissolve the residue in 1M HNO_3 and transfer the solution with the aid of 1M HNO_3 to a 100-ml polypropylene beaker so that the final volume is 15 to 20 ml. Stir the solution, insert the platinum and calomel electrodes connected to the pH meter, and observe the potential of the solution. Add 0.1N ferrous solution dropwise until the potential decreases by 200 to 300 mV (about 20 drops). (At this stage the solution will be blue if it is sufficiently pure and concentrated. If uranium is present, it is helpful to observe through a uranium glass filter.) After 10 to 15 min, if the potential has increased more than 20 mV (if the blue color has faded), add 10 drops more of the ferrous solution and wait 5 min.

Add HNO_3 until the solution volume is doubled. Observe the potential, which should be 200 to 300 mV higher than before the dilution. (The solution should now be green to yellow-green.) Add 0.07N dichromate solution dropwise until the addition of 3 drops changes the potential less than 10 mV. (About 10 drops are necessary to reach this slight excess.) In the absence of color interference, follow these oxidation state changes conveniently by observing the visual color changes. (The color changes are useful but are not necessary for the procedure.)

Ion-Exchange Separation. Add 2 to 3 ml of a resin slurry in 8M HNO_3 to each prepared sample. Stir the mixture and allow to stand for 5 min. Transfer the slurry-sample mixture to a column with the aid of about 20 ml of 8M HNO_3 . Wash the column with a total of 30 ml of 8M HNO_3 or until the wash appears colorless,

allowing the liquid level in the column to drain within 0.5 cm of the resin level before adding more acid to the column. Use a column flow rate of 1.2 to 1.7 ml/min.

Elute the Pu from the column with a total of 30 ml of stripping solution, collecting the solution in a coulometer cell. Add 2 drops of H_2SO_4 , fume the solution to dryness, and store the residue until ready to use.

Analysis. Determine an electrical calibration factor, F, by following the instruction in the coulometer manual.⁵ Determine a blank correction by the following procedure. Fill the salt bridges with 1M HNO_3 . Add to the cell 5 drops of sulfamic acid solution and then sufficient 1M HNO_3 to cover the working electrode. Stir the solution vigorously but avoid splattering. Purge the space above the solution continuously with argon at a rate of about 300 ml/min. Reduce at 0.38V vs SCE to background, about 1-9 μA . (This step usually takes from 5 to 7 min.) Oxidize at 0.91V vs SCE to about 0.5-3 μA , timing this step with a stop watch. (This step requires about 7 min.) Record the current and voltage readout. After 3.0 min additional time again record these values. Calculate the corrected readout of the blank, V_0 , by means of equation 1:

$$V_0 = E_2 - \left(\frac{E_2 - E_1}{t_2 - t_1} \right) t_2 \quad (1)$$

where E_1 and t_1 = voltage readout at first elapsed time (min), respectively;

and E_2 and t_2 = voltage readout at second elapsed time (min), respectively.

If the oxidation and reduction backgrounds noted are not obtained, clean out the cell, replace electrolyte and repeat the blank determination. Analyze the sample by the following steps. Transfer the electrolyte, the stirring bar and the cell head from the blank determination to the dry sample in the cell beaker. Begin the stirring and purging with argon. Reduce at 0.38V vs SCE until a background current of 6 to 12 μA is reached. Oxidize at 0.91V SCE to 0.5-3 μA using a stop watch as before. Record the time, current and voltage readout; 3.0 min later, again record these values. Set the coulometer to standby, stop the stirring, disassemble the cell and wash it with 1M HNO_3 so that it is ready for the next run. Calculate the corrected readout of the sample, V_1 , by means of equation (1), substituting V_1 for V_0 .

Calculate the quantity of Pu in the sample used by means of equation 2:

$$\text{Pu (mg)} = \frac{(V_1 - V_0) F}{Nc} \quad (2)$$

where V_1 = corrected sample readout, volts

V_0 = corrected blank readout, volts

F = electrical calibration factor, mg Pu/volt

and Nc = Nernst correction = 0.99987

RESULTS AND DISCUSSION

In one series of tests, 10 aliquots of plutonium standard A were each treated to adjust the oxidation state and then were subjected to the ion-exchange separation and analysis. One of these aliquots contained large amounts of Pu(VI) prepared by heating the aliquot for a long period of time with 2M HNO₃.² In all instances, the data as shown in Table I indicate that complete recovery of Pu occurred and that the precision [relative standard deviation, (RSD)] of the recovery was good.

TABLE I
RECOVERY OF PLUTONIUM USING MINI-COLUMNS

	Plutonium, mg		Recovery, %
	Taken	Found	
1	4.659	4.655	99.91
2	4.441	4.442	100.02
3	4.783	4.788	100.10
4	4.624	4.629	100.11
5	4.467	4.465	99.96
6	4.773	4.772	99.98
7	4.661	4.662	100.02
8	4.864	4.868	100.08
9	4.800	4.802	100.04
10 ^a	4.767	4.770	100.06

Average, % = 100.03

Relative Standard Deviation, % = 0.06

- a. Pretreated to generate Pu(VI) in solution prior to adjustment of oxidation state.

To evaluate the adjustment of the oxidation state in the presence of large amounts of impurities,⁴ aliquots of plutonium Standard B were spiked with metal impurities to the following concentrations relative to the plutonium:

Fe - 0.5%	Al - 1%
Mn - 0.02%	Ca - 0.1%
Mo - 3%	Cu - 0.02%
Cr - 0.5%	Mg - 0.05%
Ni - 0.2%	U - 400%

The oxidation state of each solution was adjusted and the plutonium was separated and determined as proposed. In addition, 8 aliquots without added impurities were analyzed after the conventional hydrogen peroxide adjustment of the oxidation state used routinely at NBL. The results, shown in Table II, show a Pu recovery of 99.94% and a precision (RSD) of 0.02% for the overall procedure involving the ferrous/dichromate technique of adjustment of oxidation state. The proposed overall procedure, therefore, appears to be satisfactory for the determination of Pu in the presence of the gross impurities tested.

TABLE II

RECOVERY OF PLUTONIUM IN THE PRESENCE OF IMPURITIES
AS DETERMINED BY COMPARISON TO DIRECT DETERMINATION

	Pu Found, mg/g Solution	
	<u>H₂O₂ Adjustment - No Separation</u>	<u>Proposed Adjustment - Impurities Added</u>
1	5.013	5.010
2	5.025	5.011
3	5.019	5.014
4	5.014	5.008
5	5.015	
6	5.008	
7	5.005	
8	5.015	
Average =	5.014	5.011
Relative Standard Deviation, %	= 0.12	0.02

Recovery, % = 99.94

Note: The recovery was determined by this comparison procedure because the calculated value of the standard solution was not confirmed.

A gold electrode was used in the coulometric analysis because it was easier to maintain and gave lower background currents than a platinum electrode. The method is rapid: the time required for the complete proposed separation procedure (including sample preparation and oxidation state adjustment) is 4-hr elapsed time (40-min working time) as compared to 70-hr (3-hr working time) for the macro-column separation. One analyst can complete 40 to 60 separations/day as compared to about 10/day with the macro-technique.

Future studies will consist of modifications of the cell-electrode configuration to increase the speed of analysis, and application of the method to a variety of inventory samples.

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DETECTION OF URANIUM IN ION-EXCHANGE EFFLUENTS

N. M. Trahey

Plutonium is determined at the New Brunswick Laboratory (NBL) by a constant current potentiometric method.¹ Uranium, iron, and americium are among the elements that interfere with this method and they must be removed before the determination. The separation is carried out by ion exchange. With a column of Dowex 1-X2 in the nitrate form and 8N nitric acid, plutonium is retained on the column quantitatively, while most other elements including uranium, iron and americium are not held.² When the separation is applied to uranium-plutonium sample solutions in which the uranium concentration is appreciable, the washing of the uranium from the column can be lengthy, 2 to 5 hr, and it is difficult to tell when the uranium is completely removed. Previous studies³ on the elution characteristics of uranium have relied upon emission spectrography to follow the removal of the last traces of uranium. In the present work, a simple visual colorimetric test was developed from an existing quantitative method.⁴ The procedure can detect 5 to 500 μg of uranium in a 200-ml wash volume with a minimum of pretreatment.

EXPERIMENTAL

Reagents and Apparatus

Arsenazo(III), 0.002M.

Ethylenediaminetetraacetic Acid Disodium Salt (EDTA), 0.01M

Buffer Solution. Mix equal parts of 1M triethanolamine and 0.5N HNO_3 .

Uranium Standard Solutions, 5 $\mu\text{g}/\text{ml}$ and 10 $\mu\text{g}/\text{ml}$ in 8N HNO_3 .

Test Tubes, 20 x 150 mm.

pH Paper, ranges 0 to 3 and 6.8 to 8.4.

Procedure

Pipet 20 ml of 8N HNO_3 to a 50-ml beaker. To other beakers add appropriate quantities of standard uranium solution, and add sufficient 8N HNO_3 to bring the volumes to 20 ml. In another beaker add 20 ml of the normal 200 ml of 8N HNO_3 column wash. Add to each beaker 22 ml of 7.5N NH_4OH and mix. Measure the pH with pH paper and adjust to 3 with NH_4OH or HNO_3 . Add 10 drops of EDTA, 20 drops of arsenazo(III), and 10 drops of buffer solution to each beaker and swirl. Adjust the pH to 7.5 with pH paper. Pour the

contents of each beaker into test tubes and compare the color of the "wash" solution with the blank (0 μg) and standard solutions. Multiply the estimated quantity of uranium by 10 to account for the fraction of the wash taken.

RESULTS AND DISCUSSION

Washings from a typical separation were tested with the results given in Table I. These solutions, from wash No. 7 to No. 11 showed no trace of yellow uranyl ion before the testing. It was easily determined that the washing could be stopped after No. 11 had been collected since this aliquot of the wash contained < 10 μg and, therefore, the entire 200 ml of wash contained < 100 μg of uranium. This quantity corresponds to about 0.10% error in the plutonium with a 200-mg sample. This conclusion can be made reasonably because it has been shown that the elution or washing curve of the uranium under the column conditions used does not tail badly; therefore, the No. 12 washing probably contains much less uranium than No. 11.

TABLE I
URANIUM DETECTED IN ION EXCHANGE EFFLUENTS

<u>Consecutive 200-ml Column Wash</u>	<u>Uranium Found, μg</u>
7	1000-2500
8	500-1000
9	200-500
10	100-200
11	< 100

Interference studies indicated that the EDTA is an effective masking agent for iron. Americium in the quantities normally encountered did not appear to interfere.

Color differences in the 0- to 100- μg range are easy to detect visually. Above 100 μg , the detection is more difficult. The test on each wash requires about 2 min elapsed time. The color is stable for at least 8 hr.

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ACID DISSOLUTION OF SAMPLES IN MICRO-KJELDAHL FLASKS — A PROGRESS REPORT

N. M. Trahey, A. W. Wenzel and C. E. Pietri

Improved dissolution techniques for analytical samples are continually being sought by the New Brunswick Laboratory (NBL). In the present report, the advantages of using a six-place Kjeldahl rack and flasks for the acid dissolution of U_3O_8 was investigated briefly. This type of arrangement has potential value for the acid dissolution of certain plutonium oxide and other plutonium samples that must be treated for long periods of time for complete dissolution.

After observations were made of the dissolution behavior of the U_3O_8 , the resulting solutions were analyzed for uranium by the NBL procedure¹ involving reduction with ferrous ion in phosphoric acid. These determinations were made to check on the completeness of dissolution and any loss on transfer of solution.

EXPERIMENTAL

Reagents and Apparatus

Uranium Oxide, U_3O_8 , National Bureau of Standards SRM No.950a.

Micro-Kjeldahl digestion rack and 100-ml flasks, Labconco.

Reagents and apparatus for the NBL titrimetric method are given in reference (1).

Procedure

Transfer a 250-mg sample of U_3O_8 to each of the six Kjeldahl flasks, and add 50 ml of 8N HNO_3 together with some alundum boiling chips. Adjust the heaters so that the solutions boil evenly. Replenish the acid when necessary until dissolution is complete. Transfer the solutions to 400-ml beakers for the uranium determinations.¹

RESULTS AND DISCUSSION

The dissolution time for the U_3O_8 samples was about 1 hr. A good portion of this time was needed to dissolve a slight film of U_3O_8 at the solution surface. The quantity of acid that needed to be replaced at intervals was disappointingly large. The results obtained with a set of six samples are shown in Table I. Also shown are the results obtained with four samples dissolved directly in the titration beakers.

TABLE I
RECOVERY AND DISSOLUTION TIMES

<u>Dissolution Technique</u>	<u>Time Required, min</u>	<u>Recovery, %</u>	<u>RSD, %</u>
Micro-Kjeldahl	60	99.927 - (N=6)	0.066
Beakers (unstirred solution)	60	99.960 - (N=4)	0.033

It can be seen that the Kjeldahl flasks as such present no advantages over beakers. On the other hand, it was felt certain that with refluxing action in the flasks, both the dissolution time and the quantity of acid needed would be lowered. Accordingly, U-shaped condensers were made of 4-mm o.d. tubing to extend to within 3 cm of the neck bottom. The condensers were connected in series with Tygon tubing to an air inlet rather than water because air is more convenient for glove-box use. Preliminary tests of this arrangement indeed showed marked improvement in the dissolution: no replenishment of acid was necessary and the dissolution times were now about 20 min.

Additional studies will be made in future work.

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SAFE STORAGE OF PLUTONIUM SOLUTIONS

J. R. Weiss and C. E. Pietri

At the New Brunswick Laboratory (NBL), plutonium solutions containing nitric, sulfuric or perchloric acid are stored in "storage assemblies" consisting of vented glass bottles kept in covered stainless steel containers. The solutions are so stored in order to reduce the dispersion of plutonium in case of accident. Aqueous solutions of plutonium are known to generate gases including hydrogen by radiolytic action.¹ The hydrogen gas generated is explosive in air in concentrations of 4.1 to 74% by volume.² Adequate venting of the storage assembly allows the hydrogen to dissipate before the lower concentration is reached. In the present report, an estimate was made of the hydrogen release from several venting configurations of the storage assembly to provide for safe storage of these solutions.

EXPERIMENTAL

Reagents and Apparatus

Plutonium Solutions. Solutions containing from 1 to 50 g Pu in 1 to 8M HNO_3 , about 1M HClO_4 , or less than 0.1M H_2SO_4 are generally in storage.

Solution Storage Assembly. The assembly shown in Figure 1 consists of a narrow-mouth 1-liter glass bottle with a vented vinyl stopper. The vents are holes in the stopper and they are filled with a loose plug of fiberglass to prevent loss of solution from spray. The bottle is kept in a stainless steel container when not in use. The container cover is attached to the container body with hook bolts and wing nuts. The containers are not leak-proof; in fact, the cover is fabricated to provide only a loose seal to prevent the possibility of gas pressure build-up.

RESULTS AND DISCUSSION

Hydrogen generation in Pu solutions is dependent on: (1) the kind of acid; (2) the acid concentration; (3) the Pu concentration; (4) the Pu isotopic composition. Based upon the highest specific alpha activity of the plutonium material (about 41% ^{239}Pu) received at NBL, the approximate volume of hydrogen generated in milliliters/day for 50 g Pu is estimated to be 16 for 1M HNO_3 , 32 for 1M HClO_4 and 124 for 0.1M H_2SO_4 .³

Escape of hydrogen from the storage assembly can occur by one of two mechanisms: diffusion and convection. A reasonable estimate of the hydrogen release can be made by considering the diffusion mode alone.

- A. Stainless steel container
- B. Glass bottle, 1 liter
- C. Stainless steel cover
- D. Hook bolt and wing nut
- E. Vinyl stopper
- F. Vents

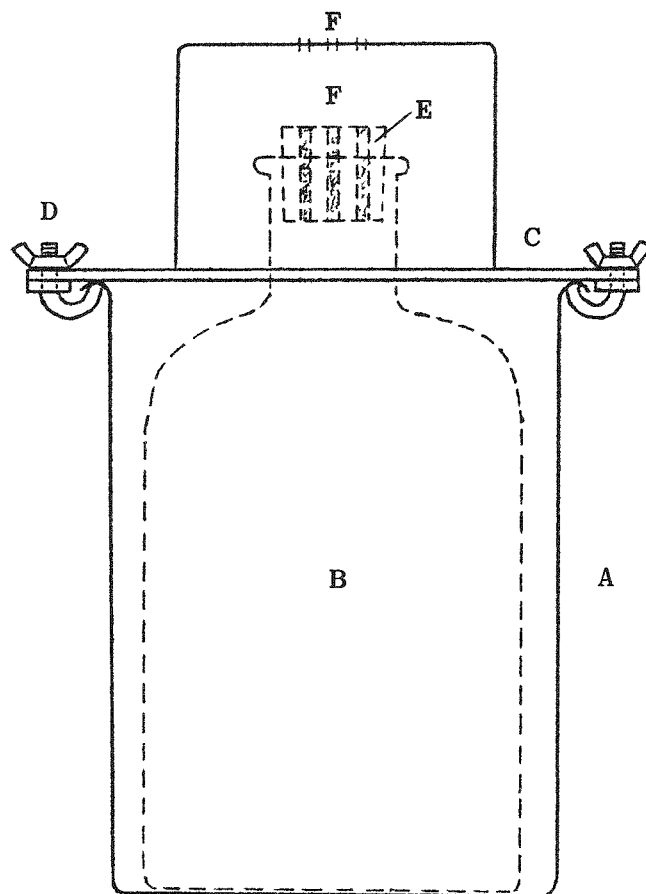


FIGURE 1. PLUTONIUM SOLUTION STORAGE ASSEMBLY

The rate of diffusion of hydrogen from a vented vessel can be calculated from equation 1:⁴

$$H_2, \text{ ml/day (STP)} = [\Delta A (d_2 - d_1) / h] 8.64 \times 10^4 \quad (1)$$

Where: A = cross-sectional area of vent, cm²

h = length of cross-sectional area of vent, cm

d₁ = concentration of H₂ outside of vessel, ml/cm³ (STP)

d₂ = concentration of H₂ inside of vessel, ml/cm³ (STP)

Δ = diffusion coefficient of H₂, 0.634 cm²/sec at 0°C,

and STP = standard conditions, 25°C and 760 mm pressure.

The diffusion coefficient of H₂ into air at 25°C is assumed to be approximately the same as at 0°C for the calculations.

In the Pu storage assembly, hydrogen diffuses out of the stopper vent of the bottle containing the Pu solution and enters the metal container from which it diffuses out via the container vent. The hydrogen diffusing out of the bottle is calculated from equation 2:

$$H_2, \text{ ml/day (STP)} = [\Delta A_b (d_2 - d_1) / h_b] 8.64 \times 10^4 \quad (2)$$

in which A_b and h_b now refer to the bottle vent dimensions, d₂ is the concentration inside the bottle, and d₁ is the concentration of hydrogen outside the bottle (inside the metal container).

Similarly, diffusion of hydrogen out of the metal container is given by equation 3:

$$H_2, \text{ ml/day (STP)} = [\Delta A_c (d_1 - d_0) / h_c] 8.64 \times 10^4 \quad (3)$$

in which A_c and h_c are now the dimensions of the metal container vent, d₀ is the concentration of hydrogen outside the container, and d₁ is the concentration inside the container.

If the storage assembly is in a well-ventilated location, e.g. 20 ft.³ closed glove box with a minimum air flow of 5 to 10 ft³/min, such that no significant concentration of hydrogen accumulates outside of the assembly, then a steady state of hydrogen concentration will be established in the bottle and container. In this case, the diffusion rate calculated from equation (2) is equal to that calculated from equation (3). Solving for d₁ the concentration of hydrogen outside the bottle and inside the metal container, one obtains

$$d_1 = H_2, \text{ ml/cm}^3 \text{ (STP)} = \frac{A_b h_c d_2 + A_c h_b d_0}{A_c h_b + A_b h_c} \quad (4)$$

Substituting this value of d₁ from equation (4) into equation (1), one obtains as the steady state of hydrogen diffusion from the

assembly:

$$H_2, \text{ ml/day (STP)} = [\Delta A_b A_c (d_2 + d_0) / (A_c h_b + A_b h_c)] 8.64 \times 10^4 \quad (5)$$

By the use of equation (5) the rate of diffusion of hydrogen from various bottle and container vent configurations of the assembly can be calculated, Table I. From these data and the hydrogen generation rates calculated previously on the basis of the solution composition, the proper venting to provide safe storage can be selected. For example, in a 0.1M H_2SO_4 solution containing 50 g Pu approximately 124 ml of H_2 is generated daily.³ Accordingly, safe venting of the storage assembly, as calculated from Table I, would be three 4-mm diam holes in the bottle vent, and three 1-mm diam holes in the steel container vent. This design provides adequate venting for up to 204 ml H_2 /day.

TABLE I

VENT CONFIGURATIONS FOR PLUTONIUM SOLUTION STORAGE ASSEMBLIES

Bottle Vent			Steel Container			H_2 Safely Vented ml/day
No. of Holes	Diam, mm	Cross Section, A_b , cm^2	No. of Holes	Diam, mm	Cross Section, A_b , cm^2	
1	4	0.1256	1	4	0.1256	106
3	4	0.3768	3	1	0.02356	204
3	5	0.5889	3	1	0.02356	262
3	5	0.5889	5	1	0.03927	327
3	5	0.5889	10	1	0.07854	402

NOTE: $d_0 = 0$; $d_2 = 0.041 \text{ ml/cm}^3$ (based upon lower explosive limit of 4.1% H_2); $h_b = 2.54 \text{ cm}$; $h_c = 0.10 \text{ cm}$; $\Delta = 0.634 \text{ cm}^2/\text{sec}$.

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