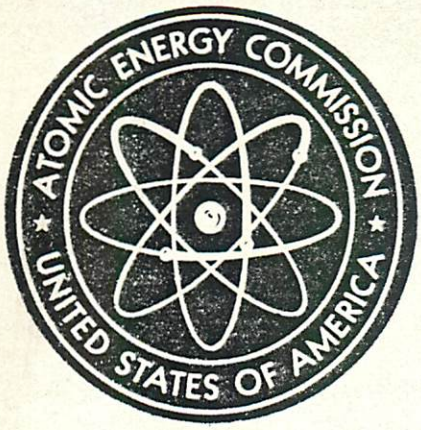

NBL-267

ANNUAL PROGRESS REPORT FOR THE PERIOD JULY 1972 THROUGH JUNE 1973

September 1973

New Brunswick Laboratory, (AEC)
New Brunswick, New Jersey

UNITED STATES ATOMIC ENERGY COMMISSION
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ANNUAL PROGRESS REPORT FOR THE PERIOD JULY 1972 THROUGH JUNE 1973

AEC Research and Development Report

NEW BRUNSWICK LABORATORY

Carleton D. Bingham, Director

September 1973

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ABSTRACTS

The Effect of Impurities on the New Brunswick Laboratory Titrimetric Method of Determining Uranium. II. Platinum Metals, Chloride and Bromide

Most platinum metals, chloride and bromide in certain concentrations interfere with the NBL titrimetric method for uranium. The elimination of the interferences is discussed.

The Effect of Impurities on the New Brunswick Laboratory Titrimetric Method of Determining Uranium. III. Fluoride

Fluoride above certain concentrations has been shown to interfere with the NBL titrimetric method for uranium. The interference can be eliminated by an evaporation step or by complexing prior to the determination of uranium.

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Evaluation of an Automatic Uranium Analyzer Based Upon Constant Current Coulometry — A Progress Report

Evaluation of the automatic uranium analyzer based upon the constant-current generation of vanadium(V) has revealed several modifications that were needed to improve the reliability of results. An unknown factor responsible for slightly negative errors still exists.

Determination of Uranium in Uranium-Thorium Solutions by Controlled-Potential Coulometry at a Mercury Pool Electrode

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Controlled-Potential Coulometric Determination of Uranium with a Platinum Electrode After Reduction with Iron(II) in Phosphoric Acid

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X-Ray Spectrographic Determination of Uranium in Low-Grade Samples by a Lithium Tetraborate Fusion Technique — A Progress Report

X-ray spectrography has been applied to the determination of uranium in low-grade residue samples. The tentative method proposed involves the use of a lithium tetraborate fusion. The experimental details and some comparative results are presented.

Non-Destructive Analysis of Low-Grade Uranium Samples by a Passive Gamma-Ray Technique

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Determination of Uranium-235 by a Delayed Neutron Counting Technique

Determination of uranium-235 in uranium dioxide-thorium dioxide mixtures and pyrocarbon- and silicon carbide-coated uranium-thorium carbide fuel beads has been carried out by bombarding with thermal neutrons and counting the delayed neutrons arising from fission of the uranium-235. The precision and accuracy of some results are given.

Preparation of Test Materials for an Interlaboratory Californium-252 Activation Analysis Evaluation Program

To evaluate the general applicability of californium-252 as a neutron source for activation analysis, an interlaboratory program was designed by Savannah River Operations involving the analysis of two materials: a 2N nitric acid solution; and a 70% silica, 20% iron oxide, 10% calcium carbonate mixture, both containing 13 elements at various levels. Details of the preparation and characterization of these test materials, carried out by NBL, are described.

Atomic Absorption Spectrophotometric Determination of Mercury in Test Materials for the Californium-252 Evaluation Program

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Dissolution of Pyrocarbon- and Silicon Carbide-Coated Uranium-Thorium Carbide Fuel Beads — Chlorination and Fusion Dissolutions

Studies on the dissolution of pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads by fusion techniques were continued. Also studied was a high-temperature chlorination technique. A proposed chlorination procedure is described.

Summary of an Interlaboratory Comparison Program on the Analysis of Pyrocarbon- and Silicon Carbide-Coated Uranium-Thorium Carbide Beads

NBL conducted an interlaboratory comparison program on the analysis of pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads. Samples of the beads from a single production lot, and synthetic uranium dioxide-thorium dioxide mixtures were analyzed for uranium by 3 laboratories by non-destructive assay techniques, and for uranium and thorium by 7 laboratories by destructive chemical procedures. The evaluation will be given in a separate report.

Mass Spectrometric Isotope Dilution Determination of Uranium and Plutonium — Volumetric vs Gravimetric Techniques for Preparing the Isotope Mixtures

The precisions of mass spectrometric isotope dilution assays of uranium and plutonium using volumetric and gravimetric preparation of the sample-tracer mixtures were compared. The preparations made by volume additions gave results essentially as precise as those made by weighing.

A FOCAL Programming System for an Isotope Ratio Mass Spectrometer Laboratory

The addition of three external FOCAL functions to enable the use of an analog to digital converter, a real time clock and a relay buffer-driver has permitted the use of the FOCAL programming system to operate the mass spectrometer installation that was formerly operated under a fixed assembly language system. The function routines, their operation and application are described.

Determination of Sensitivity Factors for the Spark Source Mass Spectrometer

Relative sensitivity factors for 70 elements in a graphite matrix were determined for a spark source mass spectrometer with electrical detection. A log-ratio scanning technique was used which yielded an average relative standard deviation of ±29% for an individual determination. By means of these factors, U_3O_8 and a synthetic mineral spiked with impurities were analyzed.

Spark Source Mass Spectrographic Determination of Impurities in Uranium Hexafluoride — A Progress Report

Progress on the development of a technique for the determination of volatile impurities in uranium hexafluoride by spark source mass spectrometry is described.

Evaluation of the Fabry-Perot Interference Spectrometer for Uranium Isotopic Analysis — A Status Report

Modifications are being made in a procedure previously described for the determination of uranium isotopic abundance by means of the Fabry-Perot interference spectrometer. These changes should speed up the analysis and may improve the precision of the results.

A Central Annunciator Panel for the New Brunswick Laboratory — A Progress Report

The various NBL alarm systems have been consolidated into one master panel in the main building with a repeater panel in the other building. The various alarms are given one of three priorities indicated by the color of the lighted display and by a distinct audio signal. The system has been in partial operation for several months.

An Automated Mini Ion-Exchange and Coulometry System — A Progress Report

To provide greater productivity two related automated systems for the determination of plutonium are under development: the ion-exchange separation of plutonium from interferences by mini-columns; the controlled-potential coulometric determination of the separated plutonium. The projects are described, their advantages are enumerated, and the status of the fabrication is outlined.

Calculation of Hydrogen Generation from Plutonium-Induced Radiolysis of Nitric, Sulfuric and Perchloric Acids

Modifications were made to an existing equation so that the hydrogen produced by radiolysis in aqueous acidic solutions of plutonium can be calculated. The calculations show that storage of plutonium in high concentrations of HNO_3 produces a smaller quantity of hydrogen than storage in H_2SO_4 or $HClO_4$ solution. The explosion hazard thus is minimized in HNO_3 solution.

A General Analytical Evaluation (GAE) Program for Uranium Hexafluoride

A new GAE program for uranium hexafluoride has been started. Phase I involving the determination of uranium content and isotopic abundance began June 1, 1973 with 20 laboratories including 11 foreign laboratories participating.

A Tentative Method for the Spectrochemical Determination of Mercury and Arsenic in a Synthetic Environmental Test Material

Existing U_3O_8 standards were used to determine mercury and arsenic in a synthetic 70% silica, 20% ferric oxide, 10% calcium carbonate matrix material containing impurities at various levels for a californium-252 evaluation program. Standards with this matrix alone were difficult to prepare. The results by the proposed procedure are compared to the quantities originally added and to the results obtained by spectrophotometric determinations.

Background Correction in Emission Spectroscopy

A simple equation is presented for correcting line intensity for background effects.

THE EFFECT OF IMPURITIES ON THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD OF DETERMINING URANIUM. II. PLATINUM METALS, CHLORIDE AND BROMIDE

J. M. Scarborough and L. Z. Bodnar

Previous reports[1-3] have discussed the interference of elements such as manganese, vanadium and mercury on the New Brunswick Laboratory (NBL) titrimetric method of determining uranium. Since these reports were issued, a systematic study of the effect of all possible impurities was undertaken, and the non-interference of copper, titanium, cobalt, nickel, cerium and samarium was demonstrated.[4] In the present work, this comprehensive study has been continued with the platinum metals, chloride and bromide.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus for the uranium determination are identical to those described in reference (1) with the exception that: (1) 100 mg of solid vanadyl sulfate dihydrate is used in place of the 10 ml of 0.05M vanadyl solution in the dilution step before titration; (2) a small amount, 1 ml, of 0.03N potassium dichromate is added to the H_3PO_4 before it is used[5]; (3) water is used as the diluent instead of 1M H_2SO_4.

Uranium Standard Solution, prepared from NBL dingot uranium.

Ruthenium Standard Solution, 10 mg Ru/ml. Dissolve 2.1 g of $RuCl_3$ in 5 ml HCl and dilute the solution to 100 ml.

Rhodium Standard Solution, 8.0 mg/ml. Dissolve 1.0 g of $RhCl_3 \cdot 3H_2O$ in water and dilute to 50 ml.

Palladium Standard Solution, 10 mg/ml. Dissolve 1.7 g of $PdCl_2$ in 30 ml of aqua regia; evaporate the solution to dryness, dissolve the residue in a small amount of 9M H_2SO_4 and dilute the solution to 100 ml with water.

Osmium Standard Solution, 10 mg/ml. Dissolve 0.85 g of $OsCl_3 \cdot 1.5H_2O$ in a few milliliters of dilute HCl, and dilute the solution to 50 ml with water.

Iridium Standard Solution, 10 mg/ml. Dissolve 0.92 g of $IrCl_3 \cdot 3H_2O$ in 6 ml of HCl, and dilute the solution to 50 ml with water.

Platinum Standard Solution, (1) 1.0 mg/ml. Dissolve 0.25 g of K_2PtCl_6 in water containing a few drops of HCl and dilute the solution to 100 ml with water.

(2) 10 mg/ml. Dissolve 0.50 g of platinum metal in aqua regia. Evaporate the solution to dryness; add 20 ml HNO_3 and evaporate to dryness; add 5 ml H_2SO_4 and a small amount of water and fume nearly to dryness; add 5 ml H_2SO_4 and a small amount of water together with 15 ml of H_3PO_4, heat until the solution is clear, and dilute to 50 ml with water.

Chloride Standard Solution, 2.0 mg/ml. Dissolve 0.33 g of NaCl in water and dilute the solution to 100 ml with water. For tests with higher concentration of chloride, use HCl.

Bromide Standard Solution, 4.0 mg/ml. Dissolve 0.52 g of NaBr in water and dilute the solution to 100 ml with water.

Procedure

Transfer to a 400-ml beaker a weighed aliquot of a uranium standard solution containing about 100 mg of uranium. In the case of the platinum group, add the appropriate quantity of standard solution of the individual platinum metal plus 2 to 5 ml of 9M H_2SO_4, and heat the solution to strong fumes of SO_3 to remove any chloride ion. Cool the solution and dilute to 15 ml with water before determining the uranium. In the halogen tests, add the appropriate quantity of halogen standard solution to the weighed aliquot of standard uranium solution and adjust the combined volume by dilution to 15 ml prior to the uranium determination. After 1 to 3 tests as indicated above, routinely determine the uranium in a weighed aliquot of the uranium standard solution containing no impurity to be assured of the proper functioning of the electrode system.

RESULTS AND DISCUSSION

Interference Effects

The data presented in Table I demonstrate the type and magnitude of the effects given by the platinum group elements. All the data obtained in the study are not shown; data sufficient to indicate the general effects are presented.

From Table I it can be seen that ruthenium, palladium, osmium, iridium and platinum cause serious positive errors in the determination of uranium by the NBL titrimetric method. Rhodium alone among the platinum metals does not cause any significant error.

Additional studies with platinum proved to be interesting. In another series of tests, not included in Table I, different results were obtained when a platinum solution prepared as described under Platinum Standard Solution (2) was used. When this platinum solution was tested, the uranium results were consistently low. In a typical experiment, 10 mg of platinum produced about a -0.5% error. This anamolous behavior requires further investigation.

TABLE I

EFFECT OF PLATINUM METALS ON NBL TITRIMETRIC METHOD

Impurity	Amount of Impurity Added, mg	U Added, mg	U Found, mg	Difference, %
Ru	10	116.91	117.40	+ 0.42
	50	116.67	121.90	+ 4.5
Rh	8	103.22	103.36	+ 0.14
	8	103.99	104.06	+ 0.07
	16	103.97	104.00	+ 0.03
	40	104.29	104.35	+ 0.06
	80	103.63	103.77	+ 0.14[a]
Pd	3	101.09	101.27	+ 0.18
	5	100.51	101.57	+ 1.0
	30	97.24	99.02	+ 1.8
Os	5	103.89	104.06	+ 0.16
	10	102.89	103.45	+ 0.54
	50	103.13	105.35	+ 2.1
Ir	5	102.90	102.97	+ 0.07
	10	102.96	103.12	+ 0.16
	20	103.75	104.08	+ 0.32
Pt	1	103.85	104.00	+ 0.14
	2	103.50	104.02	+ 0.50
	3	103.20	103.81	+ 0.59
	5	104.15	105.67	+ 1.5
	10	103.05	104.35	+ 1.3
	15	109.61	111.21	+ 1.5

a. Sluggish end point.

The effects of chloride and bromide are shown by the data in Table II. Chloride causes positive errors apparently not strictly related to the stoichiometric quantity present. In addition, chloride seriously affects the behavior of the platinum electrode. Bromide can cause either positive or negative errors depending upon the amount present. This fact suggests that there are two interfering processes occurring. One milligram or less of bromide can be tolerated.

Interference Mechanism

The mechanism of the positive interference of platinum was briefly studied. Positive errors as reported in Table I can be caused by either a dramatic shift in the end-point potential or by the presence of a reducible species capable of being oxidized by dichromate in the final diluted solution to be titrated.

Titrations in which the second-derivative technique was used to establish the exact end point showed that the presence of

platinum did not change the end-point potential of about 590 mV, and that the errors obtained by titration to the actual inflection point were of the same magnitude as those observed by titrating to a fixed potential of 590 mV. Thus, it can be concluded that the error can be attributed to the presence of a titratable species in the solution titrated rather than a shift in end-point potential.

TABLE II

EFFECT OF CHLORIDE AND BROMIDE ON NBL TITRIMETRIC METHOD

Impurity	Amount of Impurity Added, mg	U Added, mg	U Found, mg	Difference, %
Cl	1	99.37	99.55	+ 0.18
	5	98.40	98.60	+ 0.20
	15	96.61	96.96	+ 0.36
	425	91.30	91.71	+ 0.45
	850	97.58	98.57	+ 1.0
	850	98.16	100.18	+ 2.0
Br	1	108.91	108.82	- 0.08
	1	108.49	108.40	- 0.08
	1	106.69	106.70	- 0.01
	2	108.62	108.44	- 0.17
	3	107.46	107.21	- 0.23
	4	108.01	108.00	- 0.01
	4	109.49	109.43	- 0.06
	5	108.60	108.86	+ 0.24
	5	108.61	108.76	+ 0.14
	10	110.43	110.72	+ 0.26
	10	105.11	105.44	+ 0.31
	25	108.98	111.20	+ 2.0
	25	108.52	110.91	+ 2.2

A series of tests was carried out with solutions containing platinum and either no uranium or varying ratios of platinum to uranium, Table III. When platinum only, from 1 to 15 mg, is carried through the procedure, no significant blank, which would appear as uranium in a typical titration, is observed. The potential measured just prior to the start of the titration in every case was between 560 and 590 mV, and less than 1 drop of 0.03N dichromate was sufficient to increase the potential to 640 mV. However, in the presence of uranium, 5 mg of platinum causes significant positive errors. If, for example, platinum(II) is the source of the interference, it is interesting that uranium must be present in order for sufficient platinum(II) to be formed and survive the oxidation step of the procedure.

TABLE III

EFFECT OF PLATINUM IN THE PRESENCE AND ABSENCE OF URANIUM

Pt Added, mg	U Added, mg	U Found, mg	Difference, mg
1	0	< 0.06	+ < 0.06
5	0	< 0.06	+ < 0.06
10	0	< 0.06	+ < 0.06
15	0	< 0.06	+ < 0.06
0	11.47	11.49	+ 0.02
5	11.66	12.33	+ 0.67
0	21.37	21.41	+ 0.04
5	22.00	22.57	+ 0.57
0	32.84	32.86	+ 0.02
5	32.58	33.58	+ 1.0
0	108.55	108.51	- 0.04
5	108.37	109.46	+ 1.1

A spectrophotometric procedure was developed to identify platinum(II) at various stages in the titrimetric procedure. Platinum(II) in acid solution forms an extractable dithizonate; platinum(IV) does not. A brief study with this technique revealed that:

1. No platinum(II) is present in the platinum solution (No. 1) used to spike the uranium standards;

2. Platinum(IV) is not reduced to platinum(II) in the reduction step of the procedure in the absence of uranium: this fact confirms the data in Table III.

3. A large fraction of the platinum(IV) is reduced to platinum(II) in the reduction step in the presence of uranium;

4. A large fraction of the platinum(II) produced by reduction of platinum(IV) is not oxidized by the HNO_3-molybdate in the iron(II) oxidation step; it is oxidized by the dichromate titrant. In an additional study, the oxidation times for the oxidation step were increased from 3.0 min to 12 min. The platinum(II) was still not oxidized by the HNO_3-molybdate. Therefore, it is reasonable to conclude that the high results listed in Table I are caused by the presence of platinum(II) in the solution being titrated. Additional future tests will be carried out similarly with the platinum standard solution 2.

Although no tests were made to identify the oxidation states of the other platinum metals at various stages in the procedure, it is probable that these elements interfere in a manner similar to that of platinum. For example, in the case of palladium, it has been observed that finely divided metal is formed in the re-

duction step of the procedure. This metallic palladium survives the HNO_3-molybdate oxidation but is readily oxidized and dissolved by the dichromate, thereby producing high results for the uranium.

The mechanism of the chloride interference has not been studied to date in detail. With chloride present, the induction period (the time the solution is colored a deep brown-black) in the catalytic oxidation step is increased from about 30 sec to about 2 1/2 min depending on its concentration. This long induction period may indicate an interference in the oxidation step of the procedure. However, it is also possible that the main interference of chloride arises from its effect on the proper functioning of the platinum electrode, since, after exposure to chloride, the electrode must be flamed at high temperature before it can be used again. Titrations carried out by the second-derivative technique gave errors similar to those obtained with the fixed end-point procedure indicating that the presence of chloride does not affect the end-point potential.

Similarly, bromide has a serious deleterious effect on the platinum electrode behavior. After exposure to bromide in high concentrations, e.g. 10 to 25 mg in the final solution for titration, the platinum electrode must be cleaned with molten sodium carbonate and/or molten sodium bisulfate followed by cleaning in hot HNO_3. The electrode is finally ignited in a flame at high temperature and conditioned for several hours in the titration medium or ferrous sulfate solution before it can be used again. Positive errors may be due to oxidation of bromide to bromine or bromate in the final solution by the dichromate titrant. Negative errors could be caused by the formation of bromine, which can oxidize uranium(IV), in other steps in the preparation. For example, free bromine can be detected by odor just as soon as the phosphoric acid, which contains a small amount of dichromate to oxidize reducible species in the acid, is added in the procedure, and the odor persists during the entire procedure. Again, no shift in the end-point potential is observed in titrating solutions containing bromide. Additional studies with chloride and bromide are planned.

Elimination of Interferences

The platinum group metals are customarily removed from uranium sample solutions by precipitation with hydrogen sulfide in acid solution. In some cases, a double precipitation is necessary. In attempts to eliminate this gassing procedure other techniques were studied.

It was found that ruthenium and osmium can be eliminated satisfactorily by volatilization of their oxides from fuming $HClO_4$. Sample solutions are first evaporated to dryness to remove any excess HNO_3. Then, for samples containing less than 50 mg of the elements, 5 ml of $HClO_4$ and a few milliliters of water are added and the solution is heated to fumes of $HClO_4$ until the intensely colored solution changes to a pale yellow. Larger amounts can be removed by adding more $HClO_4$ and fuming longer. Samples treated in this way show no interference from these elements.

The removal of palladium and platinum can be accomplished smoothly by the copper column procedure[6] developed at NBL. In this procedure, the solution is converted to a sulfuric acid solution and then is passed through a small column of granular copper. Palladium and platinum remain on the column as metal, and uranium is eluted without loss.

At the present time, iridium must be removed by gassing with hydrogen sulfide. Rhodium, in moderate amounts, i.e. up to 80 mg in a 100-mg uranium sample, need not be removed.

Chloride and bromide are easily removed by adding 1 to 3 ml of sulfuric acid and evaporating the solution to strong fumes of SO_3.

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THE EFFECT OF IMPURITIES ON THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD OF DETERMINING URANIUM. III. FLUORIDE

L. Z. Bodnar and J. M. Scarborough

A previous report[1] on the New Brunswick Laboratory (NBL) titrimetric method of determining uranium has stated that fluoride does not interfere. This conclusion was based upon the results obtained with solutions of uranium-zirconium mixtures to which fluoride was added to keep the zirconium in solution. However, subsequent studies have shown that under certain conditions fluoride does in fact interfere. This report describes the interference of fluoride, a probable mechanism by which low results are obtained, and the elimination of the interference.

EXPERIMENTAL

Reagents, Apparatus and Procedure

The reagents, apparatus and procedure are identical to those described in reference (1) with the following exceptions: (1) 100 mg of solid vanadyl sulfate dihydrate is used instead of the 10 ml of 0.05M vanadyl solution;[2] (2) a small amount, 1 ml, of 0.03N potassium dichromate is added to the phosphoric acid before it is used to oxidize reducible material present;[3] (3) water is used as the diluent instead of 1M H_2SO_4.

RESULTS AND DISCUSSION

Effect of Fluoride. As a point of reference, a series of standard uranium solutions in 400-ml beakers was evaporated to dryness to remove most of the HNO_3 present. Then 10 ml of water and various quantities of fluoride as HF were added to each beaker. Determination of the uranium in each beaker gave the results shown in Table I. These data indicate that up to 400 mg of HF can be tolerated in the absence of free acid; larger amounts cause negative errors in excess of 0.1%.

The test was repeated with uranium aliquots containing 2 ml HNO_3, Table II. In this situation, slightly larger amounts of fluoride can be tolerated.

Similar tests were then carried out with standard uranium solutions containing zirconium (and HNO_3), the type of mixture commonly met in actual analytical samples, Table III. These data explain the earlier conclusion about the non-interference of fluoride. In the presence of 1.0 g of zirconium, which is a good complexing agent for fluoride, much larger quantities, up to about 1.5 g, of fluoride can be tolerated.

TABLE I

EFFECT OF FLUORIDE IN THE ABSENCE OF NITRIC ACID

HF Added		Relative Error, %
ml	mg	(115 mg U Titrated)
0	0	0.00
0.10	58	-0.01, 0.00
0.20	116	-0.01
0.50	289	-0.05
0.75	434	-0.09
1.00	578	-0.14
2.00	1160	-0.39
3.00	1730	-0.59
4.00	2320	-0.63

TABLE II

EFFECT OF FLUORIDE IN THE PRESENCE OF NITRIC ACID

HF Added		Relative Error, %
ml	mg	(115 mg U Titrated)
0	0	+0.02
0.10	58	-0.01
0.25	145	+0.01
0.50	289	+0.02
0.75	434	0.0
1.00	578	+0.02
2.00	1156	-0.22

TABLE III

EFFECT OF FLUORIDE IN THE PRESENCE OF ZIRCONIUM

HF Added		Relative Error, %
ml	mg	(1.0 g Zr and 55 mg U Taken)
2.0	1160	-0.01
2.0	1160	-0.01
2.5	1450	-0.09
3.0	1730	-0.27
4.0	2310	-0.76
6.0	3470	-3.5

Thus, small amounts of fluoride, less than 400 mg as HF, can be generally tolerated in the NBL titrimetric method. The amount present can be increased to about 600 mg as HF if HNO_3 is present. Above these quantities, serious errors can result unless the fluoride is complexed.

Mechanism of the Interference

It was established that 1.5 g of boric acid, a good complexing agent for fluoride, added before the analysis to a standard uranium solution containing 2 ml (1156 mg) of HF effectively eliminates the interference. Accordingly, a series of tests was carried out in which boric acid was added to uranium solutions containing fluoride at various steps in the NBL procedure. These data, Table IV, indicate that the interference occurs prior to the dilution step. Therefore, it seems likely that the uranium(IV), normally stable in the oxidation step, is being oxidized in part along with the excess iron(II) when fluoride is present.

TABLE IV

EFFECT OF BORIC ACID ADDED AT VARIOUS STEPS IN THE PROCEDURE

HF Added		H_3BO_3 Added, g	Relative Error, % (115 mg U Titrated)
ml	mg		
0	0	0	0.0
4	2310	0	-0.51
4	2310	1.5 at start	-0.04
4	2310	1.5 at reduction	-0.02
4	2310	1.5 at reduction	-0.04
4	2310	1.5 at dilution	-0.55

To test this supposition, the relative errors obtained by increasing the oxidation period (normally 3.0 minutes after the disappearance of the brown-black color) in the presence and absence of fluoride in the solution were determined, Table V. The results indeed tend to indicate that the errors caused by free fluoride are caused by premature oxidation of some uranium(IV) in the oxidation step.

One final point was checked to eliminate the possibility that fluoride interferes at least partially by shifting the end-point potential. Titrations were carried out by the second-derivative technique when fluoride was present in the solution. No significant shift in the end-point potential was observed.

Removal of Fluoride Interference

Normally, fluoride in the sample solution can be removed by a H_2SO_4- or $HClO_4$-fuming step. In some cases, however, precipitates may be formed upon fuming. In these cases, boric acid can be added to the sample solution aliquot to complex the fluoride. Table VI compares the results obtained by analyzing actual sample solutions containing excess fluoride after fuming or after adding boric acid.

TABLE V

STABILITY OF URANIUM(IV) IN THE PRESENCE OF FLUORIDE

HF Added ml	HF Added mg	Duration of Oxidation Step, min.	Relative Error, % (90-150 mg U Titrated)
0	0	3 (usual time)	0.00
0	0	10	0.00
0	0	20	-0.10
0	0	60	-0.49
4	2310	3 (usual time)	-0.39
4	2310	10	-1.13
4	2310	20	-1.49
4	2310	60	-3.09

TABLE VI

COMPARISON OF METHODS FOR ELIMINATION OF FLUORIDE INTERFERENCE

Sample,[a] NBL No.	Uranium Determined, mg/g		
	Fuming	1.5 g H_3BO_3 Added	Untreated
CS 1638	9.077	9.086	8.999
CS 1639	5.939	5.923	5.701
CS 1640	11.866	11.882	11.640
CS 1642	8.791	8.789	8.599
CS 1643	6.922	6.927	6.660
CS 1644	8.426	8.430	8.150

a. Solution obtained from actual U-Zr samples containing small amounts of fluoride from sample preparation; 4 ml HF added to each aliquot used before the determination.

REFERENCES

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

2. Eberle, A. R. and Lerner, M. W., NBL-258 (June 1971), p. 22.

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THE EFFECT OF IMPURITIES ON THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD OF DETERMINING URANIUM. IV. HYDROGEN PEROXIDE

J. M. Scarborough

Occasionally hydrogen peroxide may be used in the dissolution of certain uranium-zirconium alloys[1] or otherwise may be present in sample solutions. Although hydrogen peroxide is usually removed by evaporation or fuming steps, it is of interest to establish limits on the amount of hydrogen peroxide which can be tolerated in the New Brunswick Laboratory (NBL) titrimetric method of determining uranium.

Peroxides interfere by depleting the amount of ferrous iron added to reduce uranium(VI) to uranium(IV).

EXPERIMENTAL

Reagents, Apparatus and Procedure

In addition to the use of reagent-grade hydrogen peroxide, the reagents, apparatus and procedure are identical to those appearing in reference (1) with the following exceptions: the substitution of 100 mg of solid vanadyl sulfate for the 0.05M vanadyl solution as proposed in reference (2); the pretreatment of the H_3PO_4 with 1 ml of 0.03M dichromate as recommended in reference (3); the use of water instead of 1M H_2SO_4 for the diluent.

RESULTS AND DISCUSSION

The data obtained from the titration of known amounts of uranium mixed with known amounts of hydrogen peroxide are shown in Table I.

As expected, the results of the study indicated that hydrogen peroxide does not interfere with the NBL titrimetric method if the number of milliequivalents of iron(II) exceeds by an appreciable amount the total milliequivalents of hydrogen peroxide and uranium(VI).

It should be noted that insufficient iron(II) is indicated by the absence of the dark brown coloration which follows the addition of the HNO_3-molybdate oxidizer solution. When this condition is reached, the data show that serious interference from hydrogen peroxide occurs. Normally, failure to observe the dark coloration during the oxidation step is sufficient reason to discard a sample and to determine the cause of the failure. Thus, it is unlikely that a sample containing excessive amounts of peroxide would be titrated unknowingly.

TABLE I

EFFECT OF HYDROGEN PEROXIDE ON THE NBL TITRIMETRIC METHOD FOR THE DETERMINATION OF URANIUM

Milliequivalents Added			Uranium, mg		Difference, mg
H_2O_2	U(VI)	Fe(II)	Added	Found	
0	0.8	5	100.82	100.80	-0.02
0.018	1.0	5	115.84	115.81	-0.03
0.09	1.0	5	115.43	115.40	-0.03
0.18	1.0	5	117.36	117.30	-0.06
1.8	1.0	5	116.94	116.97[a]	+0.03
2.7	1.0	5	116.54	b,c	--
3.2	1.0	5	116.48	113.51[b]	-2.6
3.2	0.8	10	97.64	97.59	-0.05
3.6	1.0	5	115.40	b,c	--
3.6	0.8	10	97.66	97.72	+0.05
5.4	1.0	5	117.07	c,d	--
9.0	1.0	5	115.75	c,e	--

a. Very light brown color on addition of HNO_3-Mo oxidizer

b. No color on addition of oxidizer.

c. Titration not performed.

d. Color at reduction indicated a small amount of U(VI) remains.

e. Color at reduction indicates most of U(VI) remains.

REFERENCES

1. Eberle, A. R., Lerner, M. W., Goldbeck, C. G. and Rodden, C. J., NBL-252 Part I (July 1970), p. 6.

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3. Ibid., p. 14.

ELIMINATION OF SOME INTERFERENCES IN THE NEW BRUNSWICK LABORATORY TITRIMETRIC URANIUM METHOD BY MEANS OF A COPPER COLUMN

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

Mercury, platinum and palladium have been shown to interfere with the New Brunswick Laboratory (NBL) titrimetric method of determining uranium.[1,2] These elements can be removed by precipitation with hydrogen sulfide; mercury can also be separated by reduction with stannous chloride.[1] A new method, involving the use of a copper column to reduce these elements to the metallic state, has been developed. This technique accomplishes both the reduction and separation in one step. Thus, it is faster, simpler and less subject to error than the previous procedures described.

EXPERIMENTAL

Reagents and Apparatus

Copper Column. The reduction column is prepared by filling a Bio-Rad disposable polyethylene column, 0.7 cm ID by 4 cm high, with reservoir, to a depth of about 3.0 cm with electrolytic copper granules of about 50 mesh. The column is washed with a few milliliters of 10% H_2SO_4 before it is used.

Mercury Solution, 16.4 mg/ml, prepared by dissolving mercury metal in 1:1 HNO_3 and diluting the solution to volume.

Platinum Solution, 1.0 mg/ml (solution No. 1), and 10 mg/ml (solution No. 2), prepared as in reference (2).

Palladium Solution, 10 mg/ml, prepared by dissolving $PdCl_2$ in aqua regia, evaporating the solution to dryness, dissolving the residue in 9M H_2SO_4, and diluting the resulting solution to volume.

The reagents, apparatus and procedure for the NBL titrimetric method are as described in reference (3) except that: 100 mg of solid vanadyl sulfate is used in place of the 0.05M vanadyl solution in the dilution step;[4] 1 ml of 0.03M dichromate is added to the H_3PO_4 before it is used;[5] and water is used as the diluent instead of 1M H_2SO_4.

Procedure

Add 5 to 7 ml of 9M H_2SO_4 to a weighed sample solution aliquot and evaporate the mixture to light fumes of SO_3. Cool the solution and dilute to about 25 ml. Add the solution to the copper column. When the column flow stops, wash the beaker and column once with a 10-ml portion of 10% H_2SO_4 and twice more with 10-ml portions of 2% H_2SO_4. Finally, wash with 10 ml of water. Evaporate the combined effluents on a steam bath to a small volume and dilute to 15 ml.

(The final solution should contain less than 5 ml of H_2SO_4.) Determine the uranium in the usual manner. Use $HClO_4$ in place of the H_2SO_4 if so desired.

Removal of Mercury

RESULTS AND DISCUSSION

Two series of 7 uranium standard solutions each containing aluminum and mercury were prepared as given in the procedure with either H_2SO_4 or $HClO_4$ being used. The results of the uranium determinations are shown in Table I.

TABLE I

REMOVAL OF MERCURY[a] ON A COPPER COLUMN PRIOR TO URANIUM DETERMINATION

Relative Difference from Prepared Value of Uranium, %			
H_2SO_4 Medium		$HClO_4$ Medium	
-0.10	-0.04	+0.16	+0.03
-0.04	+0.08	-0.01	-0.03
+0.08	+0.01	+0.07	+0.07
+0.02		+0.05	

a. Solutions contained 61 to 91 mg of uranium, about 300 mg of aluminum and 75 mg of mercury.

To evaluate the limitation of the amount of mercury that the column will remove, another series of solutions containing uranium, aluminum and increasing amounts of mercury was treated and analyzed, Table II. It is apparent that the column technique will separate at least 240 mg of mercury, a quantity far greater than is normally present in actual sample aliquots.

TABLE II

COLUMN CAPACITY FOR REMOVAL OF MERCURY

Mercury Present,[a] mg	Relative Difference from Prepared Value of Uranium, %
80	-0.02
80	+0.03
160	+0.05
160	+0.01
240	+0.02
240	+0.06
560	+0.12
560	+0.13

a. Solutions to be analyzed contained 61 to 102 mg uranium plus 5 g $Al(NO_3)_3 \cdot 9H_2O$ in 10% HNO_3 in addition to the mercury. The H_2SO_4-fuming preparation was used.

Table III presents results obtained both by the stannous chloride separation technique and proposed procedure on actual uranium-thorium dissolver solutions containing 15 to 20 mg of mercury per aliquot.

TABLE III

ANALYSIS OF URANIUM-THORIUM DISSOLVER SOLUTIONS CONTAINING MERCURY BY STANNOUS CHLORIDE AND COPPER COLUMN TECHNIQUES

Sample No.	Concentration of Uranium in Sample, mg/g	
	Stannous Chloride	Copper Column
1	1.33, 1.34	1.34, 1.34
2	1.42, 1.44	1.42, 1.42
3	1.36, 1.38	1.38, 1.37
4	1.22, 1.25	1.23, 1.23
5	1.35, 1.35	1.36, 1.36
6	1.57, 1.59	1.60, 1.60
7	1.59, 1.60	1.62, 1.62
8	1.68, 1.68	1.72, 1.71
9	1.48, 1.47	1.51, 1.51

Removal of Platinum and Palladium

Preliminary results with solutions containing platinum or palladium treated by the proposed procedure indicate that up to 10 mg of each can be removed from a solution containing 100 mg of uranium. One modification that appeared to be necessary in the column preparation was the addition of a 1-cm depth of filter pulp below the copper granules. This layer of filter pulp aids in the removal of finely divided platinum or palladium metal that is not held by the copper column. These studies are continuing.

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APPLICATION OF THE RADIOMETER TITRATOR MODEL TTT2 TO THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD OF DETERMINING URANIUM

L. Z. Bodnar and J. M. Scarborough

The Radiometer Titrator TTT2 is an instrument that automatically titrates a solution to either a preselected potential or pH. Accurate approach to the end point is controlled by means of a "proportional band", an adjustable span of potentials or pH values prior to the end point within which the titrant delivery rate is controlled by the Titrator. Under Titrator control, the titration proceeds by incremental addition, each new increment being smaller and each interval between increments being longer. Thus, the end point is approached gradually after an initial period of rapid titrant addition.

This instrument is potentially useful in applying the New Brunswick Laboratory (NBL) titrimetric method[1] of determining uranium both in the manual and automatic mode. The goals of this study were to assess the basic reliability of the Titrator in titrating uranium solutions according to the NBL method, and to learn of any modifications needed to improve its performance.

EXPERIMENTAL

Reagents and Apparatus

The reagents for the titrimetric procedure are identical to those given in reference (1) with the following exceptions: (1) 100 mg of solid vanadyl sulfate dihydrate is used in place of the 10 ml of 0.05M vanadyl solution in the diluent; (2) 1 ml of 0.027N dichromate is added to the H_3PO_4 before it is used; (3) water is used as the diluent instead of 1M H_2SO_4.

Radiometer Titrator (London Company) Model TTT2, equipped with magnetic valve MNV-1, and 50-ml gravity buret with fine tip.

Balance, top-loading Mettler Model P162, with gravimetric titration accessory Model DP11.

Procedure

Prepare the solution to be titrated in the usual manner by reducing the uranium to uranium(IV) with ferrous ion in H_3PO_4, oxidizing the excess ferrous ion with HNO_3 and molybdate catalyst, diluting with water, and adding solid vanadyl sulfate. Insert the platinum and calomel electrodes, position the solution so that the buret tip is under the surface, and activate the Titrator.

To titrate 50 to 150 mg of uranium, use the following instrumental settings:

Range = mV x 1

Titration Selector = downscale

End Point = 580 mV

Proportional Band Width = 200 mV

Delay of Shut Off = 15 sec

Buret Rate of Delivery = 10 ml/min

RESULTS AND DISCUSSION

Instrumental Settings

The instrument settings listed above were selected on the basis of the recommendations given by the manufacturer and a large number of exploratory titrations with standard uranium solutions. In the volumetric mode, the delivery rate of the buret is controlled by both the buret-tip opening and an adjustable set screw on the magnetic buret control. A rate of 10 ml/min was selected because the delivery of 50 ml, the buret capacity, would take somewhat under 6 min: about 4 min for continuous delivery and less than 2 min for the intermittant (proportional-band) delivery. This 6-min period is within the maximum time of 7 min that can be taken in a titration without the possibility of incurring a negative error.[1]

The proportional-band width setting is adjusted to allow about 80% of the titrant to be added without interruption; the remaining 20% is then added under the control of the Titrator. With a 200-mV proportional-band width and the cut-off potential at 580 mV, the Titrator will generally control the addition of titrant, when more than 50 mg of uranium is present, after about 80% of the titrant has been added and the registered potential is 380 mV. However, in cases in which less than 50 mg of uranium is present, control may begin much earlier because the electrode potential of the initial solution may be very close to 380 mV. A setting of 300 mV for the band width would cause the titration to be under the Titrator control right from the beginning of the titration, even in the presence of large amounts of uranium, causing the titration to be unduly prolonged. With a 100-mV setting for the band width, the Titrator control would take over only a few tenths of a milliliter before the actual end point and overshooting would undoubtedly occur. There are no adjustment settings between these values.

When the preselected end-point potential is reached, a "delay of shut-off" circuit is activated which blocks the delivery of titrant for a preselected period. When the potential remains at or above the end-point potential for the preselected period of time, the "delay of shut-off" circuit turns off the instrument. The 15-sec delay time was chosen arbitrarily; the rapid estabishment of equilibrium near the end point makes this setting non-critical. Longer periods made no difference in the results.

The end-point setting of 580 mV was selected on the basis of the volumetric results with standards, Table I. With this cut-off potential, very little overshooting of the actual end point of 590 to 600 mV occurs. Previous work[1] has shown that this actual end-point potential is reasonably independent of the composition of the sample solution provided the H_3PO_4 concentration remains constant. Thus, mixtures of uranium with aluminum, niobium, zirconium, thorium, stainless steel elements, and beryllium all have this identical end point. (Increasing the volume of H_3PO_4 in the procedure from 40 to 65 ml as is used for uranium-plutonium sample solutions[2] to help keep the plutonium from precipitating does affect the end-point potential, increasing it to about 610 mV.)

TABLE I

EFFECT OF CUT-OFF POTENTIAL AND DICHROMATE CONCENTRATION ON TITRATION

Dichromate Concentration, N	Uranium Titrated, mg	Cut-Off Potential, mV	Average Final Potential, mV	Relative Difference, %[a]
0.027	100	570	610	-0.07, -0.10, +0.01, +0.01, -0.06, -0.07, -0.02, -0.09, -0.12
	100	580	625	+0.02, +0.03, -0.03, -0.07, 0.00, +0.03, -0.02, 0.00, +0.08
	100	590	635	+0.09, +0.11, -0.06, +0.06, +0.03, +0.08
	50	580	645	-0.02, +0.08, +0.08, -0.01, +0.07, +0.01
0.010	50	580	605	-0.29, -0.25, -0.27, -0.19
	50	590	615	-0.09, -0.11, 0.00, -0.01
	50	600	625	0.00, -0.02, -0.06, -0.02, +0.02
	50	610	640	+0.14, +0.17, +0.22, +0.20, +0.17

a. $\left(\frac{\text{Determined-Actual}}{\text{Actual}}\right) \cdot 100.$

With 0.01N potassium dichromate in the titration of quantities of uranium below 50 mg, the optimum cut-off potential appears to be near 600 mV, Table I. Again there is little overshoot of the potential, but it is unfortunate that the end-point setting must be changed with the use of the more dilute dichromate.

With 0.027N dichromate and the 580 mV cut-off potential, the reliability of the titration was studied with niobium, stainless steel elements, aluminum, thorium, zirconium, and fluoride (complexed with boric acid) added to about 100 mg of uranium, Table II. All of the relative differences obtained between the determined value and the amount of uranium taken can be seen to be within 0.10% and most are within 0.05%. The results of one group do not differ significantly from the others.

TABLE II

EFFECT OF IMPURITIES ON THE TITRATION[a]

Impurity	Quantity, mg	Relative Difference, %
0	0	-0.07, +0.01, -0.02, +0.03
Nb	100	-0.02, +0.06, -0.04, +0.03, -0.07
Stainless steel[b]	500	+0.05, -0.03, -0.05, +0.03
Al	100	-0.01, -0.04, +0.02, +0.02
Th	750	-0.08, -0.02, -0.03, +0.01
Zr	100	-0.06, -0.07, +0.03, -0.07
HF (+ H_3BO_3,1 g)	(2 ml)	-0.03, -0.01, -0.04, +0.01

a. 100 mg uranium titrated

b. No. 304 (18% Cr, 8% Ni, ~ 74% Fe)

Table III lists the results obtained with the gravimetric titration apparatus. The same concentration of dichromate titrant, 0.027N, was used throughout to evaluate the levels of uranium that can be titrated without changing the end point cut-off potential. It can be seen that from about 40 to 350 mg can be titrated with the same setting, 580 mV. Again it is unfortunate that for less than 40 mg of uranium, the cut-off potential must be shifted to another value, 550 mV. The lower cut-off potential is necessary to prevent overshooting the end point when titrating with 0.027N dichromate. This observation is in contrast to the case discussed earlier in which the cut-off potential was raised when titrating with 0.01N dichromate.

The reliability of the Titrator was further assessed by the analysis by the volume technique of actual analytical samples containing a fairly constant quantity, 84 to 133 mg, of uranium, Table IV. These samples were also analyzed by a different analyst by the conventional NBL manual procedure.

TABLE III

URANIUM ANALYSES WITH GRAVIMETRIC BURET AND CONSTANT DICHROMATE CONCENTRATION

Cut-Off Potential, mV	Uranium, mg		Difference, %
	Added	Found	
580	349.473	349.242	-0.07
	335.876	335.540	-0.10
	226.693	226.483	-0.09
	219.598	219.546	-0.02
	122.967	122.955	-0.01
	113.086	113.093	+0.01
	98.048	98.038	-0.01
	85.468	85.543	+0.09
	82.187	82.151	-0.04
	80.449	80.416	-0.04
	79.898	79.961	+0.08
	75.824	75.894	+0.09
	75.432	75.410	-0.03
	52.739	52.794	+0.10
	53.719	53.761	+0.08
	42.457	42.474	+0.04
	42.630	42.693	+0.15
580	24.420	24.501	+0.33
570	21.604	21.735	+0.61
560	21.390	21.426	+0.17
550	31.795	31.813	+0.06
	31.835	31.823	-0.04
	20.238	20.246	+0.04
	21.405	21.403	-0.01
	11.337	11.345	+0.07
	10.591	10.603	+0.11

TABLE IV

COMPARISON OF RESULTS OBTAINED MANUALLY AND WITH TITRATOR

NBL Number	Sample Type	Uranium Titrated, mg	Uranium, g/g	
			Manual	Titrator
EU-19410	uranyl nitrate	84	0.2131, 0.2131	0.2130, 0.2131
EU-19411	UO_2	113	0.8710, 0.8712	0.8712, 0.8709
EU-19658	U-Zr scrap	95	0.00971, 0.00971	0.00970, 0.00970
EU-19666	U-Al	133	0.01303, 0.01302	0.01303, 0.01303
EU-19667	U scrap	114	0.01099, 0.01098	0.01098, 0.01097
EU-19668	U scrap	107	0.01730, 0.01729	0.01730, 0.01730
EU-19669	U scrap	130	0.01600, 0.01600	0.01599, 0.01601
EU-19555	UO_2	107	0.8783, 0.8785	0.8784, 0.8789
EU-19956	UO_2	104	0.8787, 0.8787	0.8793, 0.8786
EU-19965	UO_2	117	0.8782, 0.8790	0.8790, 0.8783
EU-19687	U-Al	91	0.1461, 0.1461 0.1461	0.1463, 0.1465

This study indicates clearly that the Titrator can titrate uranium solutions prepared by the NBL method with essentially the same reliability as obtained by a careful analyst carrying out the titration conventionally to a preselected potential provided the quantity of uranium is within certain limits. It also indicates that the Titrator (especially in the gravimetric mode) should be capable of being used in an automated apparatus such as the Automatic Uranium Analyzer (Dichromate).[1] In such a case, the cupped noble metal electrode responsible for the "seeking" action, previously found to be necessary in the Analyzer to slow down the titrant delivery as the end point is approached,[1] would be unnecessary. This modification would be a distinct advantage because the "seeking" action is difficult to adjust and is the weakest point of the Analyzer. Accordingly, an automatic uranium apparatus based upon the Radiometer Titrator is being constructed for evaluation.

The study also indicates that the possibility of making two modifications in the Titrator should be investigated. In the first place, it would be advantageous to slow down even more the rate of addition of titrant near the end point. Secondly, it would be helpful to be able to use a proportional band of 150 mV, a span of potentials in between the 100 mV and 200 mV now on the instrument. These changes should help speed up some analyses and prevent overshooting the actual end point in other cases in which small amounts, < 50 mg, of uranium are titrated with either 0.01N or 0.027N dichromate.

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EVALUATION OF AN AUTOMATIC URANIUM ANALYZER BASED UPON CONSTANT CURRENT COULOMETRY — A PROGRESS REPORT

C. G. Goldbeck, M. W. Lerner and G. E. Peoples

In a previous report,[1] an automatic uranium analyzer based upon titration with electrogenerated vanadium(V) was described. Preliminary data were given of results obtained shortly after the automation of the entire instrument was completed. The present report is concerned with the continued evaluation that is being made before the instrument is used on a routine basis.

It had been shown that problems with the generating platinum gauze electrode could arise that lead to high results after a short series of determinations. The specific cause was not determined but it was found that the problem could be avoided by using an electrode with large surface area, by generally limiting the quantity of uranium to be titrated to < 130 mg, and by leaving the generating electrode in a reducing solution when not in use.

Another difficulty that appeared was a gradual decrease in sensitivity of the platinum sensing electrode, which could result in positive errors. Although sensitivity would be restored for a short time after the electrode was cleaned and fired, the electrode frequently became increasingly sluggish after a few runs. This lack of sensitivity, which causes overshooting of the end-point potential, could be seen as a gradual climbing of the potential of a sample, after the first cut-off point, to the end-point potential without the need for any current pulsing. When the usual pulsing technique was used near the end point, the registered potential never caught up with the actual potential and serious errors resulted. Again, this behavior could be observed by stopping the pulsing at some point and watching the potential drift past the end point with no additional current being applied.

In studies[2] being carried out at the New Brunswick Laboratory (NBL) on the interference of various impurity elements on the manual NBL titrimetric method, it was shown that chloride has a deleterious effect on the platinum sensing electrode. To eliminate the possibility that chloride leakage from the calomel electrode caused this gradually increasing sluggish response of the sensing electrode, a potassium sulfate salt bridge was applied to the calomel electrode. This precaution improved the performance of the platinum electrode. It now holds its sensitivity, and may actually improve after the first few runs of the day.

Another factor affecting the instrumental performance was recognized: the position of the platinum sensing electrode with respect to the generating electrode. This position was found to be critical in obtaining a satisfactory cut-off of the continuous current before the pulsing begins. In certain positions, there

occurs a large (20 to 25 mV) jump, up or down, in the potential when the current flow stops. The platinum electrode is normally lined up along side of the reference electrode to maintain a fixed distance between the two. To orient the platinum wire with respect to the generating electrode, both the calomel and platinum wire are rotated. This adjustment is now facilitated by the use of a rigid plastic reference electrode holder with a slot in the outer shell for the wire. This holder is simply rotated to position the platinum wire correctly without disrupting the reference-sensor electrode distance.

It was also shown in the previous report[1] that a negative bias of 0.2 to 0.3% seemed to appear frequently. This error was found to be lessened by the use of diluent cooled to < 10°C. However, even after this precaution was incorporated later into the procedure, a slight (0.1 to 0.2%) negative bias presisted.

This 0.1 to 0.2% negative bias was believed at first to be caused by the presence of vanadium(V) in the diluent as reported in reference (3). However, tests by a spectrophotometric procedure[4] failed to show any significant vanadate in the diluent which is made up fresh every day.

Recent work attempting to resolve this problem centered on removing the electrodes from the influences of the atmosphere above the reacting solution during the oxidation step in which large quantities of oxides of nitrogen are evolved in a fine spray of solution. Some analyses were made by adding the reagents manually away from the electrodes, and then putting the beaker in the instrument and lowering the electrodes for the titration. In 11 runs, 9 were within 0.07 sec of the theoretical 100- to 200-sec results. The other 2 were 0.12 and 0.15% high, not low.

With these results in mind, another gauze electrode was tried which was narrower than the previous electrode and consequently could be suspended higher above the solution during the reactions. No improvement in the negative bias resulted.

An attempt was then made to add the reagents to a beaker one position before the titrating position. In this situation, a magnetic stirrer was to be used to stir the reacting solution. This approach was temporarily abandoned when it was found that the magnetic stirring, with the stirrer base located beneath the turntable, was too difficult to control for smooth mixing of the solution.

Another approach was then studied that involved blowing a fast stream of nitrogen down on the surface of the reacting solution during the entire operation. In the first trial of this study only 1 of 16 runs exceeded 0.1% of the theoretical value. More data will be accumulated on this modification. It is hoped that whatever step is eventually necessary to eliminate the negative bias will at the same time make it possible to eliminate the necessity of cooling the diluent.

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DETERMINATION OF URANIUM IN URANIUM-THORIUM SOLUTIONS BY CONTROLLED-POTENTIAL COULOMETRY AT A MERCURY POOL ELECTRODE

K. Lewis

Uranium in graphite- and silicon carbide-coated uranium-thorium carbide nuclear fuel bead samples is determined routinely at the New Brunswick Laboratory (NBL) by the NBL titrimetric method.[1] This method generally requires 50 to 250 mg of uranium. It was desirable to have an alternative method available that could determine smaller quantities, about 10 mg, with the same reliability of within 0.10% precision and accuracy.

The controlled-potential coulometric determination of uranium at a mercury pool has been shown to be a reliable method.[2-4] Uranium should be readily determined by this technique in uranium-thorium solutions since thorium is not electroactive at the potential used for the reduction of uranium and thus should not interfere. The method was evaluated by analyzing uranium-thorium mixtures.

EXPERIMENTAL

Reagents and Apparatus

Sulfamic Acid Solution, saturated.

Standard Uranium Solution, prepared by weight from NBL dingot uranium metal, 99.972% uranium.

Standard Thorium Solution, prepared from reagent-grade thorium nitrate tetrahydrate.

Coulometer, M-T Controlled-Potential Coulometer System, Model 3, with cell as in reference (4).

Working Electrode, mercury, double-distilled.

Reference Electrode, saturated calomel (SCE).

Nitrogen, high-purity, dry.

Procedure

Place 7 ml of mercury in the cell. Add 5 to 7 ml of 0.5M or 1.0M H_2SO_4, 5 drops of sulfamic acid solution, and the weighed aliquot of sample solution. Assemble the cell and pass nitrogen over the solution surface for 10 min. Pre-reduce at +0.085V vs SCE until a background current of 5 to 10 μa is attained. Turn off the coulometer and adjust the potential to -0.325V vs SCE.

Zero the integrator and start the reduction and a timer. Continue the reduction until a steady low background current of about 10 μa is attained. At this point begin recording the integrator readout and time at 3 to 5 min intervals. When the change in readout per unit time, ΔQ, is constant, record a final readout and time.

Multiply ΔQ by the titration time and subtract the product from the final integrated readout to obtain the readout corrected for the continuous background current. Run a blank without uranium in the same manner. Calculate the uranium quantity from the corrected readout by means of the electrical calibration factor of the instrument and Faraday's law in the usual way.

RESULTS AND DISCUSSION

The precision and accuracy of determining uranium in the absence of thorium were first established. For 6 determinations of about 10 mg of uranium each, the relative standard deviation (RSD) was 0.02% and the recovery 100.00%.

Initial coulometric determinations on uranium-thorium mixtures with U:Th ratios of 1:5 gave relatively lower initial currents, longer runs and lower recoveries than those without the thorium. The electrolyte, therefore, was changed from 0.5M to 1.0M H_2SO_4. This change improved the run behavior and the uranium recovery. The results of a series of determinations obtained with the 1M H_2SO_4 are shown in Table I.

TABLE I

ANALYSIS OF A URANIUM-THORIUM SOLUTION[a]

Uranium, mg		
Taken	Found	Recovery, %
9.7536	9.7488	99.95
9.0478	9.0435	99.95
9.7408	9.7336	99.93
9.3839	9.3764	99.92
9.6418	9.6292	99.87
9.7107	9.7023	99.91
	Average, %	99.92
	RSD, %	0.04

a. U:Th ratio of 1:5.

Although these results are generally satisfactory, they indicate that thorium may in fact affect the determination to a small degree despite the fact that it is not electroactive at these potentials. Accordingly, determinations were made of solutions in which the U:Th ratio was increased, Table II.

TABLE II

ANALYSIS OF URANIUM-THORIUM SOLUTIONS[a]

U:Th Wt. Ratio	N	Uranium Recovery, %	RSD, %
(U alone)	7	99.97	0.06
1:5	8	99.93	0.03
1:10	4	100.01	0.02
1:20	4	100.13	0.09

a. 10 mg U taken.

These results indicated that the method is reliable with U:Th ratios at least as high as 1:10.

To determine if the slightly high results obtained with a ratio of 1:20 was due to the increased viscosity of the solution, a final series of runs were made with a smaller amount of uranium, 2 mg, and a U:Th ratio of 1:25. These solutions were less viscous than the previous set. The data, shown in Table III, reveal that the viscosity apparently does cause the slightly high results obtained previously. These meager data, however, are not conclusive.

TABLE III

ANALYSIS OF URANIUM-THORIUM SOLUTION (U:Th OF 1:25) CONTAINING LESS URANIUM[a]

U:Th Wt Ratio	N	Uranium Recovery, %	RSD, %
(U alone)	7	100.07	0.06
1:25	6	100.11	0.02

a. 2 mg uranium taken.

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CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM WITH A PLATINUM ELECTRODE AFTER REDUCTION WITH IRON(II) IN PHOSPHORIC ACID*

K. Lewis and M. W. Lerner

The Davies and Gray[1] method of determining uranium involves reduction of the uranium to uranium(IV) by iron(II) in strong phosphoric acid solution, oxidation of the excess iron(II) by nitric acid and molybdate catalyst, dilution of the phosphoric acid medium with water, and titration of the uranium(IV) with potassium dichromate.

In the present work, it was found that the uranium(IV) produced by these reactions can be determined by controlled-potential coulometry with a platinum electrode. After the dilution step, the uranium(IV) is allowed to react with the iron(III) present in the solution to produce iron(II) which is then oxidized coulometrically. The volumes of reagents are appropriately scaled down so that all the reactions take place in the conventional coulometric cell.

The results obtained for 5 to 10 mg of uranium have a relative standard deviation of within 0.1%. With an electrical calibration, a negative bias of about 0.2% exists; therefore, a chemical calibration must be used to obtain accurate results. The reason for the bias is being sought at the present writing.

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X-RAY SPECTROGRAPHIC DETERMINATION OF URANIUM IN LOW-GRADE SAMPLES BY A LITHIUM TETRABORATE FUSION TECHNIQUE — A PROGRESS REPORT

A. J. Busch and C. G. Goldbeck

X-ray spectrography has the potential to analyze quickly and inexpensively those low-grade residue samples which for reasons of small quantity and inhomogeneity should not be analyzed by the highly precise and accurate New Brunswick Laboratory (NBL) titrimetric method. Moreover, these samples are generally difficult to dissolve, and total dissolution of the fairly large samples required for wet chemical analysis is tedious and slow. In these cases, X-ray spectrographic analyses may be satisfactory if the determination is faster and less tedious than the titrimetric method, and if the accuracy and precision are within 10%.

In the present study the lithium tetraborate fusion[1] technique was used. Refinements added to the basic fusion procedure involved the addition of lithium carbonate[1] to ensure better mixing in the melt, the addition of an absorber such as lanthanum oxide[2] to obtain more uniform matrices, and better casting details such as the use of high fusion temperatures and the use of graphite casting rings and block. These factors plus a more efficient measurement procedure involving a higher voltage on the target tube and a rotating sample holder gave results that appeared to be promising.

EXPERIMENTAL

Reagents and Apparatus

Lanthanum Oxide, 99.999% pure.

Lithium Tetraborate, 99.99% pure.

Lithium Carbonate, analytical reagent.

Graphite Crucibles, 2 1/4 in. long x 1 1/4 in. OD and 1 in. ID.

Graphite Casting Block and Retaining Rings, 1 1/4 in. OD and 1 in. ID.

Mixer Mill, Spex Industries.

Plastic Vials, 60 ml, with 3/8 in. diameter plastic mixing ball.

Electric Furnaces, one to be used at 1100°C, one at 600°C.

X-ray Spectrograph, Norelco, inverted optics with four-sample chamber, a target tube operated at 50 kV and 20 mA in an air path together with a lithium fluoride analyzing crystal and a scintillation counter with a thallium-activated sodium iodide crystal operated at 0.75 kV. A single-channel pulse-height analyzer is adjusted to a base-line of 0.50 V with a window-width of 3.00 V.

Procedure

Fused Disk Preparation. Place about 10 g of sample in a plastic vial with plastic ball, and mix in a mixer mill for 5 min to break up any lumps and homogenize the sample. Place the following materials into a fresh plastic vial containing a plastic mixing ball: 100.0 mg of sample; 1.00 g of lanthanum oxide; 0.64 g of lithium carbonate; and 8.00 g of lithium tetraborate. Shake the vial for 5 min in the mixer mill. Transfer the mixture to a graphite crucible and place the crucible in a furnace at 1100°C. After 5 min remove the crucible, swirl it well, and return it to the furnace. Place the graphite casting block and ring in the 600°C furnace. After 10 min, remove the block and ring and place them on a transite sheet. Remove the crucible from the furnace and pour the melt into the ring resting on the block. Allow to cool to room temperature. Dislodge the ring to obtain the prepared disk.

Measurement. Mount the disk in the rotating specimen holder so that the plane side is measured. Count the uranium L_α peak at a 2θ of 26.14°, and the background on both sides of the peak at 25.14° and 30.14° for 100 sec each. Calculate the net L_α count by subtraction of a weighted background equal to 3/4 of the 25.14° intensity plus 1/4 of the 30.14° intensity in the usual manner. Determine the uranium concentration from a calibration curve prepared from standards, either previously analyzed by wet chemical analysis or synthetically prepared, counted in an identical manner.

RESULTS AND DISCUSSION

The recommended procedure is based upon many exploratory tests designed to improve the homogeneity of the prepared disk and to minimize the effects of differences in sample composition. Other preliminary tests indicated that reliable measurements could be obtained by using the target tube voltage and the background correction technique proposed.

The calibration curve of net uranium counts/sec vs uranium concentration is essentially linear up to 5% uranium for the particular type of residues analyzed. These residues consists chiefly of silicates and oxides and may contain calcium, aluminum, niobium, zirconium, iron and other elements in addition to the uranium.

A comparison of the X-ray spectrographic results and wet chemical results obtained by two different laboratories including NBL on a group of residue samples is shown in Table I. The wet chemical data indicate that the samples may not have been completely homogeneous. With this factor in mind and considering the small samples used here, the average X-ray spectrographic data with a few exceptions agree fairly well with the wet chemical values. The agreement between the duplicate X-ray spectrographic results is

rather poor. This poor precision is due in part to the small net counts obtained in addition to the use of small samples of a somewhat heterogeneous nature. Future work will involve attempts to obtain more homogeneity in the materials to be analyzed, and the use of a polished disk face and longer counting times to improve the reproducibility. The applicability of the standard addition or internal standard techniques to this particular type of sample may also be investigated.

TABLE I

COMPARISON OF X-RAY SPECTROGRAPHIC RESULTS
WITH WET-CHEMICAL RESULTS

Sample No.	Uranium, g/g				
	X-Ray			Wet Chemical (Titrimetric)	
	(1)	(2)	Average	NBL	Other
1	0.0063	0.0072	0.0068	0.0069	0.00813
2	0.0064	0.0067	0.0066	0.0075	0.00876
3	0.0072	0.0078	0.0075	0.0079	0.00797
4	0.0061	0.0069	0.0065	0.0063	0.00710
5	0.0106	0.0116	0.0111	0.0109	0.0116
6	0.0131	0.0131	0.0131	0.0130	0.01314
7	0.0061	0.0061	0.0061	0.0064	0.0075
8	0.0070	0.0067	0.0069	0.0064	0.00737
9	0.0034	0.0025	0.0030	0.0053	0.0062
10	0.0079	0.0085	0.0082	0.0094	0.0092
11	0.0068	0.0068	0.0068	0.0066	0.00753
12	0.0062	0.0065	0.0064	0.0070	0.0080
13	0.0078	0.0082	0.0080	0.0097	0.0103
14	0.0086	0.0082	0.0084	0.0083	0.0090
15	0.0068	0.0063	0.0066	0.0063	0.0067
16	0.0086	0.0078	0.0082	0.0103	0.00995
17	0.0106	0.0103	0.0105	0.0102	0.01049
18	0.0070	--	0.0070	0.0065	0.00765
19	0.0067	--	0.0067	0.0070	0.00753
20	0.0058	--	0.0058	0.0063	0.00715
21	0.0069	--	0.0069	0.0083	0.00954
22	0.0112	0.0112	0.0112	0.0112	0.01208

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NON-DESTRUCTIVE ANALYSIS OF LOW-GRADE URANIUM SAMPLES BY A PASSIVE GAMMA-RAY TECHNIQUE

R. C. Hagenauer, C. L. Zyskowski and L. C. Nelson, Jr.

The application of reliable non-destructive analysis (NDA) techniques for the determination of uranium-235 is one of the projects currently being undertaken by the New Brunswick Laboratory (NBL). The application of NDA to low-grade uranium samples is one phase of this project. Analysis of these samples by highly precise and accurate wet chemical methods is generally unwarranted for three reasons: they are often not homogeneous, and sampling errors may far outweigh the advantages of accurate measurements; the concentration of uranium in the total quantity of material represented by the sample may be small, thus the intrinsic value of the material may be low; and the dissolution of the sample is generally slow and tedious.

General NDA methods that have been used for the analysis of nuclear fuels include fission-neutron coincidence counting,[1] and 14-MeV-neutron activation[2] or thermal-neutron activation with fission-product gamma-ray counting.[3] These methods either are not applicable to the types of samples mentioned above because of a lack of sensitivity, or they involve variables that significantly decrease the reliability of the analyses.

Gamma-ray spectrometry has been used extensively at NBL for the analysis of low-grade samples in the past.[4,5] Correction for self-absorption, however, has always presented a problem. The decay of uranium-235 to thorium-231 is accompanied by the emission of an intense gamma ray with an energy of 185.7 keV. Since this energy is relatively low, attenuation by the typical sample to be analyzed is significant. In the present study, a technique involving ytterbium-169[6] has been applied to obtain this correction. In this technique, the attenuation of a pair of gamma rays from ytterbium-169 which bracket the energy of the gamma ray from uranium-235 is observed. The quantitative measurement of the uranium-235 gamma ray and the determination of its attenuation correction are the basic factors in the proposed method.

EXPERIMENTAL

Apparatus

Vials, polystyrene, 22 mm OD x 12 mm high, and 39 mm OD x 12 mm high. (The larger vial, used for samples of low uranium-235, can accommodate nearly four times as much sample as the smaller vial. The smaller vial is adequate for most samples.)

Counting Equipment. A Ge(Li) detector with a cobalt-60 gamma-ray efficiency of 4% relative to a 3 x 3 in. NaI detector, and a

resolution of 1.32 keV at the 185.7-keV gamma ray was used in conjunction with an 8192-channel analog-to-digital converter interfaced to a PDP-15 computer. A block diagram of the electronic configuration is shown in Figure 1.

Procedure

For a series of measurements on similar samples, proceed as follows:

(1) select a sample with a uranium-235 concentration that gives a count rate approximating the average activity of the series;

(2) adjust the pulser frequency to a value within a factor of five of the 185.7-keV gamma-ray peak activity;

(3) select a ytterbium-169 source so that the intensities of the 177.2- and 198.0-keV peaks are also within a factor of five of the intensity of the 185.7-keV peak;

(4) adjust the counting time so that at least 10,000 counts at the uranium-235 peak will be collected;

(5) when the correct pulser frequency has been established, record a spectrum of the pulser only;

(6) with an empty vial in place, take a blank count of both the ytterbium-169 source and the pulser;

(7) with a vial containing a sample in place, collect the spectral data for ytterbium-169, uranium-235 and the pulser; for each series of samples count a standard sample to check the overall counting electronics;

(8) finally, determine the height of the sample in the vial with the vial on its side.

Acquire the data and calculate peak areas by means of two computer programs. Use the PHA4K[7] program to acquire data in 1024 channels of computer memory. Accumulate data from four spectral areas (4K data area) and store on magnetic tape. At a later time, retrieve the data, compute and read out the peaks of interest by means of the peak-fitting program GASPAN.[8]

RESULTS AND DISCUSSION

Pulser Correction. The variable frequency pulser shown in Figure 1 is used to correct for detector pile-up. As the count rate increases, the percentage of counts lost increases. The decrease in the pulser count rate is a measure of this loss. The correction can differ by 7% between standards and samples.

Geometry Correction. The size of the sample is variable. Assuming that all the activity is coming from a point source at the center of the sample, it can be seen that as the sample volume in the vial increases, the distance from the point source to the detector will increase and the solid angle subtended by the detector will decrease.

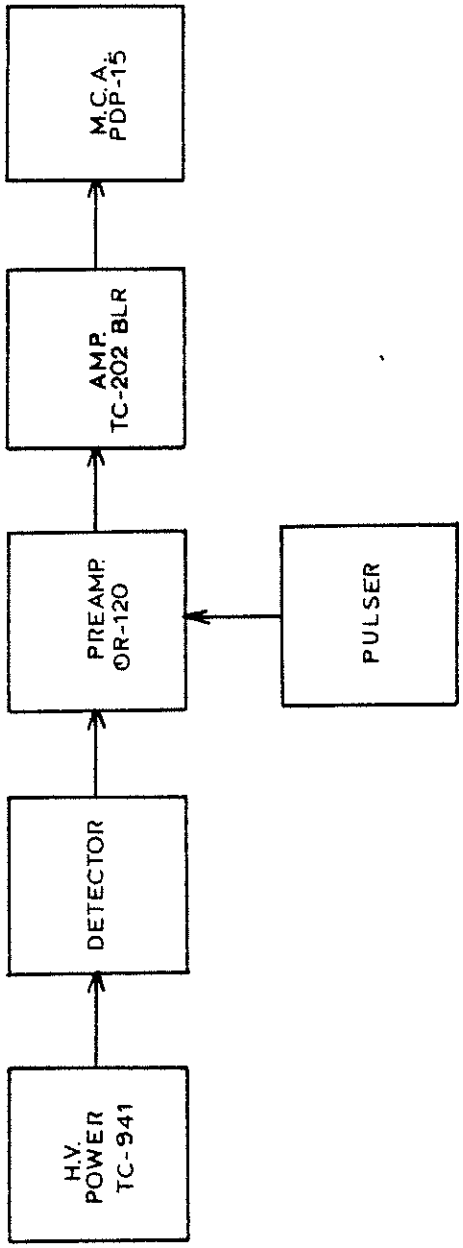

FIGURE 1. GAMMA-RAY COUNTING APPARATUS

Since the vial is a thin cylinder, it is easier to measure the sample volume by placing the vial on its side and measureing the sample height perpendicular to the plane which is tangent to the vial circumference rather than measuring the sample height along the central axis. In this way small volume differences between samples become more apparent. The height of a sample measured this way is related to the volume by the equation:

$$V_S = h\left[\left(T - \frac{d}{2}\right)\left(dT - T^2\right)^{\frac{1}{2}} + \frac{d^2}{4}\left(\sin^{-1}(x) + \frac{\pi}{2}\right)\right] \quad (1)$$

where V_S = sample volume, mm^3;

h = thickness (height) of vial, mm;

d = diameter of vial, mm;

T = measured height of sample, mm;

and $x = \left[\left(T - \frac{d}{2}\right)/\frac{d}{2}\right]$;

The heights can be measured reproducibly to 0.5 mm. A computer program was used to calculate the actual volume at 0.5-mm height intervals. The fraction of the vial capacity occupied by the sample can then be calculated by dividing the sample volume by the total volume of the vial:

$$Cf = V_S/V_V = \text{capacity fraction} \quad (2)$$

where V_V = volume of empty vial, mm^3;

$= \pi d^2 h/4$.

A preliminary peak efficiency for the 185.7-keV gamma ray was estimated. After correcting the observed peak counts for gamma-ray attenuation, the geometry factor, GF, was determined by the use of standards from the following equation:

$$GF = \frac{Pe}{\text{observed C/sec} \cdot \text{mg } ^{235}U} \quad (3)$$

where Pe = peak efficiency of counting system, in units of $\frac{C}{\text{sec} \cdot \text{mg } ^{235}U}$

and C = counts

The Cf vs GF was then plotted and a linear least squares fit through the points was computed. Since the GF must approach 1 as the sample volume approaches 0, the slope was forced to go through the origin by correcting the estimated gamma-ray peak efficiency. This corrected peak efficiency thus is a more accurate value for the actual peak efficiency for the counting system. These data are shown in Table 1 and Figure 2. The scatter of the points in Figure 2 is believed to be due to some inhomogeneity of the (synthetic) standard samples.

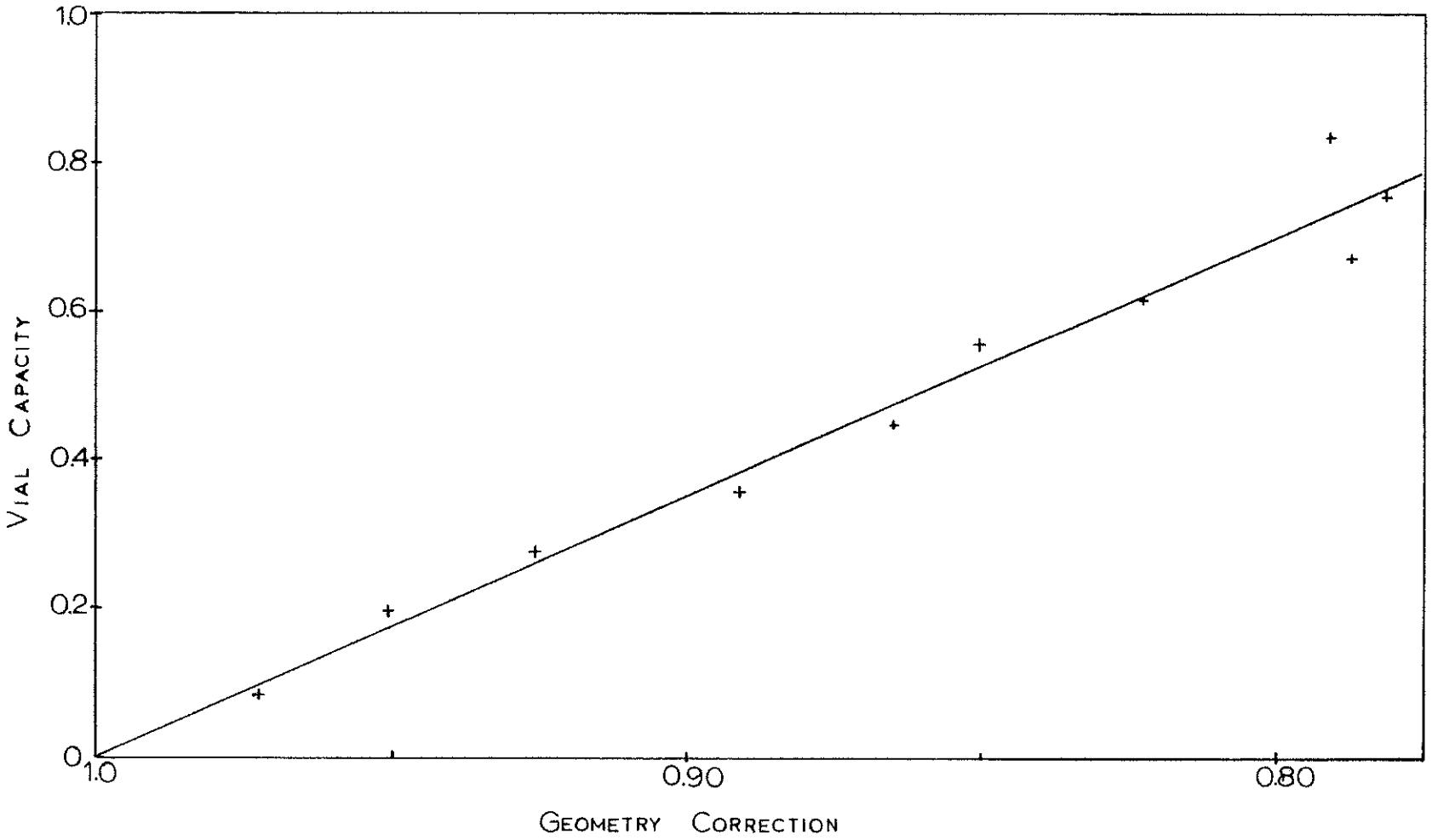

FIGURE 2. CORRECTION FOR GEOMETRY EFFECTS OF SAMPLE SIZE

TABLE I

VARIATION OF GEOMETRY CORRECTION WITH CAPACITY FRACTION

Sample Height, mm	Capacity Fraction	Geometry Correction
3.0	0.081	0.972
5.5	0.195	0.951
7.0	0.273	0.926
8.5	0.356	0.891
10.0	0.442	0.864
12.0	0.557	0.850
13.0	0.615	0.823
14.0	0.671	0.787
15.5	0.753	0.782
17.0	0.829	0.792

Self Absorption. Since the 185.7-keV gamma ray is of low energy, it is absorbed significantly within the sample according to the following equation:

$$A = A_o e^{-\mu x} \tag{4}$$

where A = measured activity of the sample, counts;

A_o = true activity (at zero self-absorption), counts;

μ = linear absorption coefficient of the sample matrix, mm^{-1};

and x = distance through the sample which uranium-235 gamma rays must travel, mm.

The attenuation by the sample was measured by the ytterbium-169-source technique.[6] The ytterbium-169 isotope has 177.2-keV and 198.0-keV gamma rays that bracket in energy the 185.7-keV gamma ray of uranium-235. Consequently, the average ytterbium-169 attenuation is an estimate of the attenuation of the radiation from uranium-235. Since the assumption has been made that the activity of the uranium-235 arises from the center of the material, and since the ytterbium-169 is placed on top of the material in the vial, its gamma rays must pass through twice as much material as the uranium-235 gamma rays. Attenuation (Att) of ytterbium-169 can then be represented by the relationship:

$$Att = \frac{A_o}{A} = e^{2\mu x} = e^{b} \tag{5}$$

where $b = 2\mu x$.

The ytterbium-169 attenuation was calculated by counting the ytterbium-169 source through an empty vial previous to counting the standard. Since, on the average, uranium-235 gamma rays travel only half the distance travelled by ytterbium-169 gamma rays, its attenuation can be approximated by the following calculation:

$$Att_{(^{169}Yb)} = e^{b} \tag{6}$$

therefore,

$$b = \ln\left[Att_{(^{169}Yb)}\right] \tag{7}$$

Let

$$c = b/2$$

therefore,

$$e^{c} = Att_{(^{235}U)} \tag{8}$$

Standards of known uranium-235 content were prepared in different matrices of different densities and average atomic number. Pulser and vial capacity corrections were made for each count. Both ytterbium-169 and uranium-235 attentuation factors were determined experimentally. Attenuation factors for the uranium-235 standards were determined by comparing the measured gamma activity to the amount of uranium-235 gamma activity expected after correction for geometry and detector peak efficiency. Table 2 lists the experimentally determined attenuation factors for ytterbium-169 and uranium-235. The attenuation factors for uranium-235 were also calculated using the expressions derived above (equations 4 to 8) in combination with the experimental values of $Att_{(^{169}Yb)}$. The solid line in Figure 3 represents a least squares fit of the relationship between $Att_{(^{169}Yb)}$ and $Att_{(^{235}U)}$ for different matrices. Most of the points obtained by counting uranium-235 standards (appearing as points on graph) fall close to the line of the theoretical slope. It is not yet known why the standards containing a natural uranium matrix show greater deviations.

Analysis of Samples. The quantity of uranium-235 is calculated using the detector peak efficiency as follows:

$$^{235}U,\ mg = \frac{(P)(PF)(G)}{(H)(Pe)(t)} \tag{9}$$

where P = peak area, counts(c);

PF = pulser correction factor;

G = gamma-ray attentuation factor (Figure 3);

H = geometry correction factor (Figure 2);

Pe = peak efficiency of counting system, $\frac{C}{sec \cdot mg\ ^{235}U}$;

t = counting time, sec.

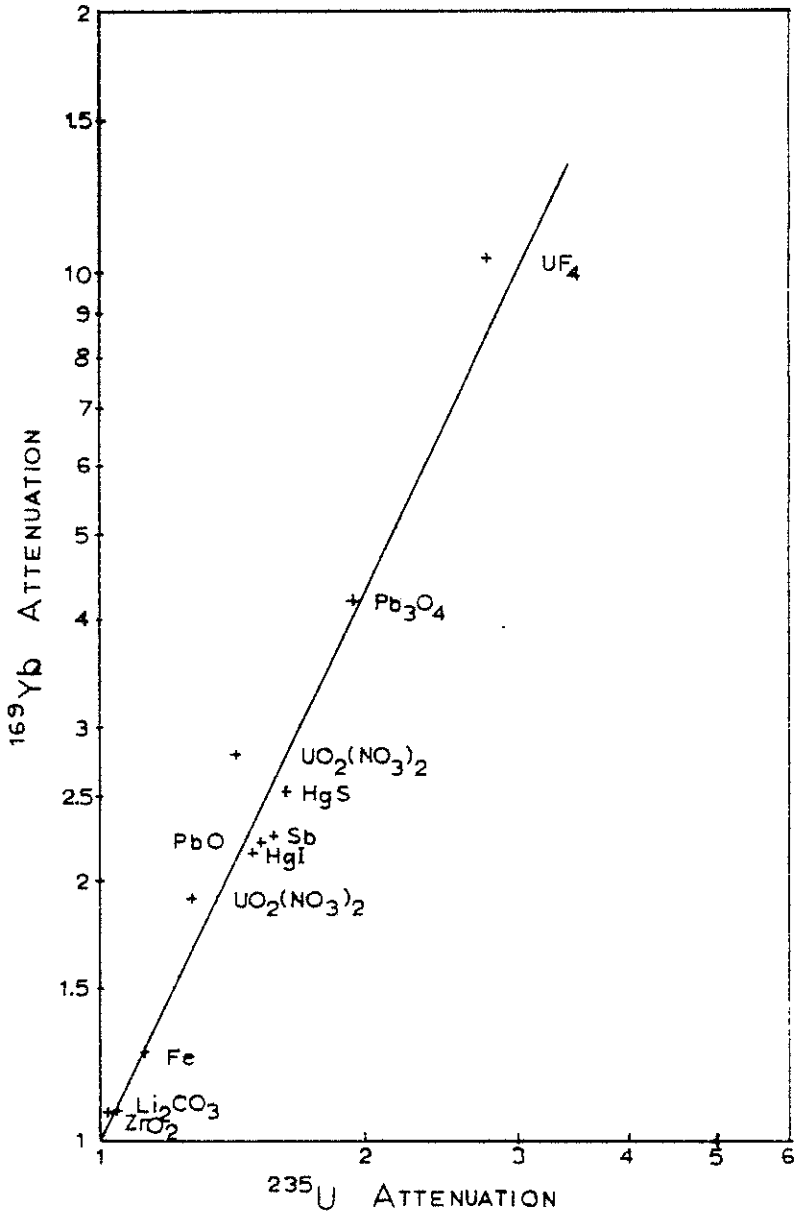

FIGURE 3. CORRECTION FOR GAMMA-RAY ATTENUATION

TABLE II

URANIUM-235 GAMMA-RAY ATTENUATION WITH VARIOUS MATRICES

Sample Matrix	Attenuation Factors	
	Average ^{169}Yb	^{235}U
$UO_2(NO_3)_2$	1.90	1.27
HgI	2.16	1.49
Fe	1.26	1.12
Li_2CO_3	1.08	1.01
Sb	2.20	1.51
UF_4	10.35	2.76
$UO_2(NO_3)_2$	2.80	1.43
Pb_3O_4	4.20	1.94
HgS	2.53	1.62
	2.50	1.63
Pb_3O_4	4.13	2.04
PbO	2.25	1.58
ZrO_2	1.08	1.04

A set of data obtained for actual samples is shown in Table III. The activity range is typical of the usual residue or scrap sample received at NBL for analysis. The attenuation corrections are small because of the small quantities of samples used. The agreement of less than 1% between duplicate samples indicates the reliability of the attenuation and sample height correction factors and also the homogeneity of the samples. In Table IV, the total uranium results calculated on the basis of the isotopic abundance values are given together with the chemical values obtained by another laboratory. (Chemical values obtained by NBL are not available at the present time.)

TABLE III

ANALYSIS OF CALCINED ASH RESIDUES[a]

Sample	Counts				Correction Factors			Corrected ^{235}U Counts ^{235}U	^{235}U, mg/g Sample
	^{169}Yb-198.0 keV	^{169}Yb-177.2 keV	^{235}U-185.7 keV	Pulser	Height	Average ^{169}Yb Attenuation	^{235}U Attenuation		
1-1[b]	99,056	67,929	16,693	53,853	0.9647	1.019	1.010	18,235	4.78
1-2	98,116	68,694	32,691	52,792	0.9144	1.013	1.006	38,941	5.04
2-1[b]	98,706	68,575	18,296	53,716	0.9514	1.014	1.007	20,262	5.24
2-2	96,815	67,438	34,183	53,510	0.9066	1.018	1.014	40,164	5.20
3-1[b]	96,956	66,641	19,734	53,372	0.9582	1.031	1.015	22,024	5.70
3-2	98,141	67,673	37,490	53,288	0.9066	1.015	1.008	43,953	5.69
4-1[b]	98,021	68,060	19,940	53,472	0.9514	1.017	1.008	22,214	5.76
4-2	99,007	68,355	38,270	53,474	0.9066	1.009	1.005	44,579	5.77
5-1[b]	98,025	67,407	16,611	53,569	0.9709	1.023	1.012	18,160	4.70
5-2	98,908	67,773	30,875	53,185	0.9222	1.009	1.004	35,537	4.60
6-1[b]	97,980	67,942	21,417	53,355	0.9582	1.015	1.008	23,729	6.14
6-2	97-498	67,020	40,762	53,437	0.9144	1.026	1.013	47,509	6.15

a. Counting time = 1800 sec; pulser blank = 56216 counts; ^{169}Yb-198.0 keV blank = 100628 counts; ^{169}Yb-172.2 keV blank = 68852 counts, pulser (^{169}Yb count) = 53614 counts.

b. 0.5-g sample; others 1-g samples.

TABLE IV

COMPARISON OF NDA AND CHEMICAL RESULTS IN SAMPLES

Sample	U, mg/g	
	NDA	Chemical
1-1	5.20	5.35
1-2	5.55	--
2-1	5.77	5.89
2-2	5.73	--
3-1	6.28	6.11
3-2	6.27	--
4-1	6.32	6.21
4-2	6.36	--
5-1	5.18	5.29
5-2	5.07	--
6-1	6.76	6.75
6-2	6.77	--

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DETERMINATION OF URANIUM-235 BY A DELAYED NEUTRON COUNTING TECHNIQUE

R. C. Hagenauer, C. L. Zyskowski and L. C. Nelson, Jr.

Determination of the uranium-235 content of samples weighing up to 20 g has been carried out by bombarding with thermal neutrons and counting the delayed neutrons arising from fission of the uranium-235. Standards containing uranium-235 are treated in the same manner. Because of the high thermal-neutron cross section of uranium-235, self-absorption is an important factor in the analysis, especially in samples such as pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads which have relatively high local concentrations of uranium-235.

EXPERIMENTAL

Apparatus

Vials, polystyrene, 16 mm OD x 55 mm high.

Neutron Source. The thermal-neutron source assembly consists of a 250-μg californium-252 source placed in the center of a beryllium block 6 in. x 6 in. x 8 in. surrounded by 10 in. of paraffin. A hole 2 in. in diameter is drilled through the paraffin and beryllium to within 2 in. of the californium-252 source, Figure 1. In this hole is placed a sample vial holder made from a 2-in. diameter lucite rod with a 9/16 in. hole down the center. This combination of beryllium and plastic gives an even flux distribution along the sample and a fairly high degree of moderation.

Counting Equipment. The neutron counter consists of thirty 20-in. long helium-3 detector tubes placed in 3 concentric circles around a 2-in. diameter well to provide an absolute efficiency of 40%.[1] Pulses from the detectors are amplified and counted on NIM scaler equipment. An additional pulse discriminator circuit is used to reject gamma-ray pulses. Ten seconds after the vial is removed from the neutron source, a microswitch located in the assembly automatically initiates the counting by activating a timer. The scaler count and sample identification number are printed and punched on paper tape by an attached teletype for subsequent computer reduction. A block diagram is shown in Figure 2.

Procedure

Place a weighed sample in a sample vial, position the vial in the neutron source assembly, and bombard for 2 min. Transfer the vial manually to the neutron detector well and take a 200-sec count 10 sec after removal from the neutron source.

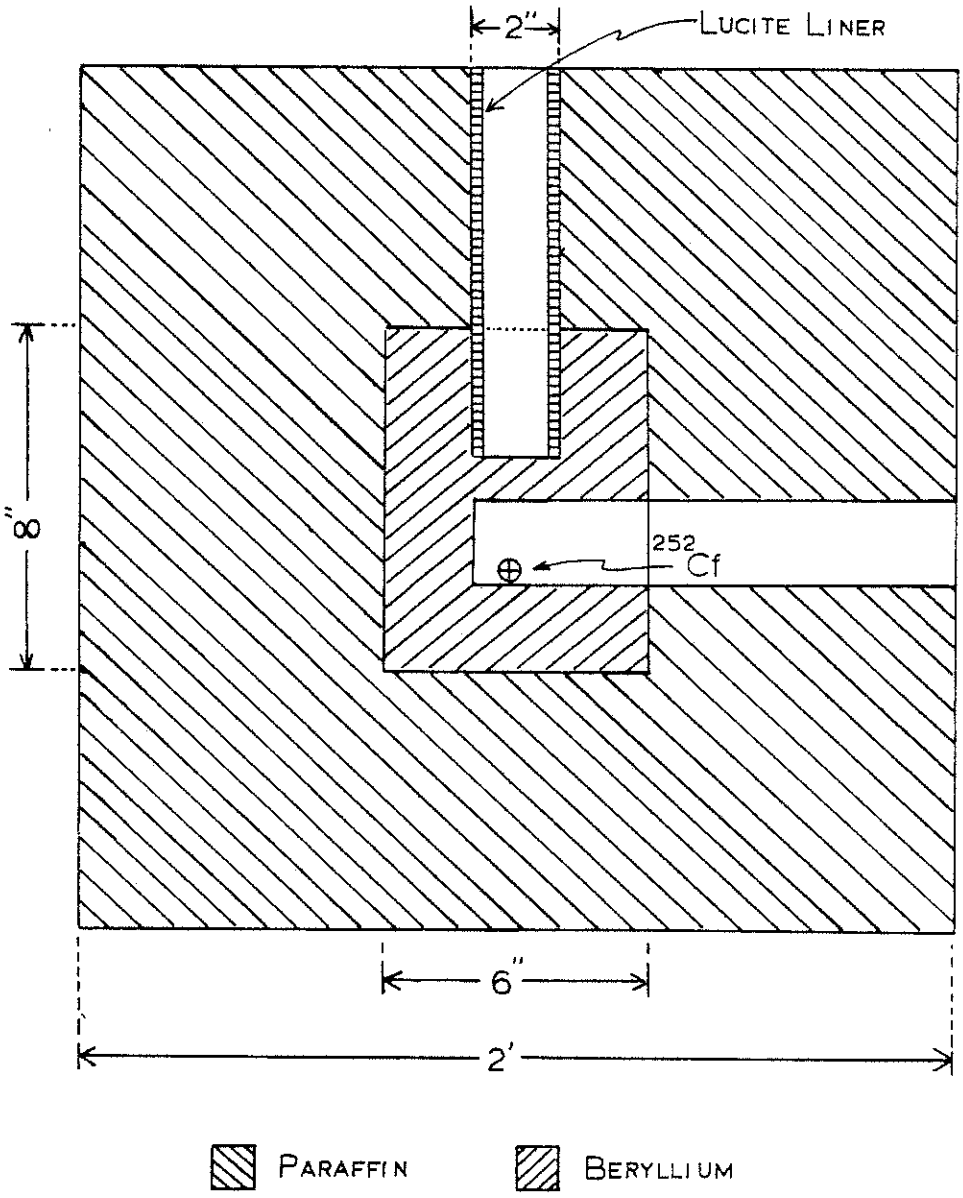

FIGURE 1. CALIFORNIUM-252 BOMBARDMENT CONFIGURATION

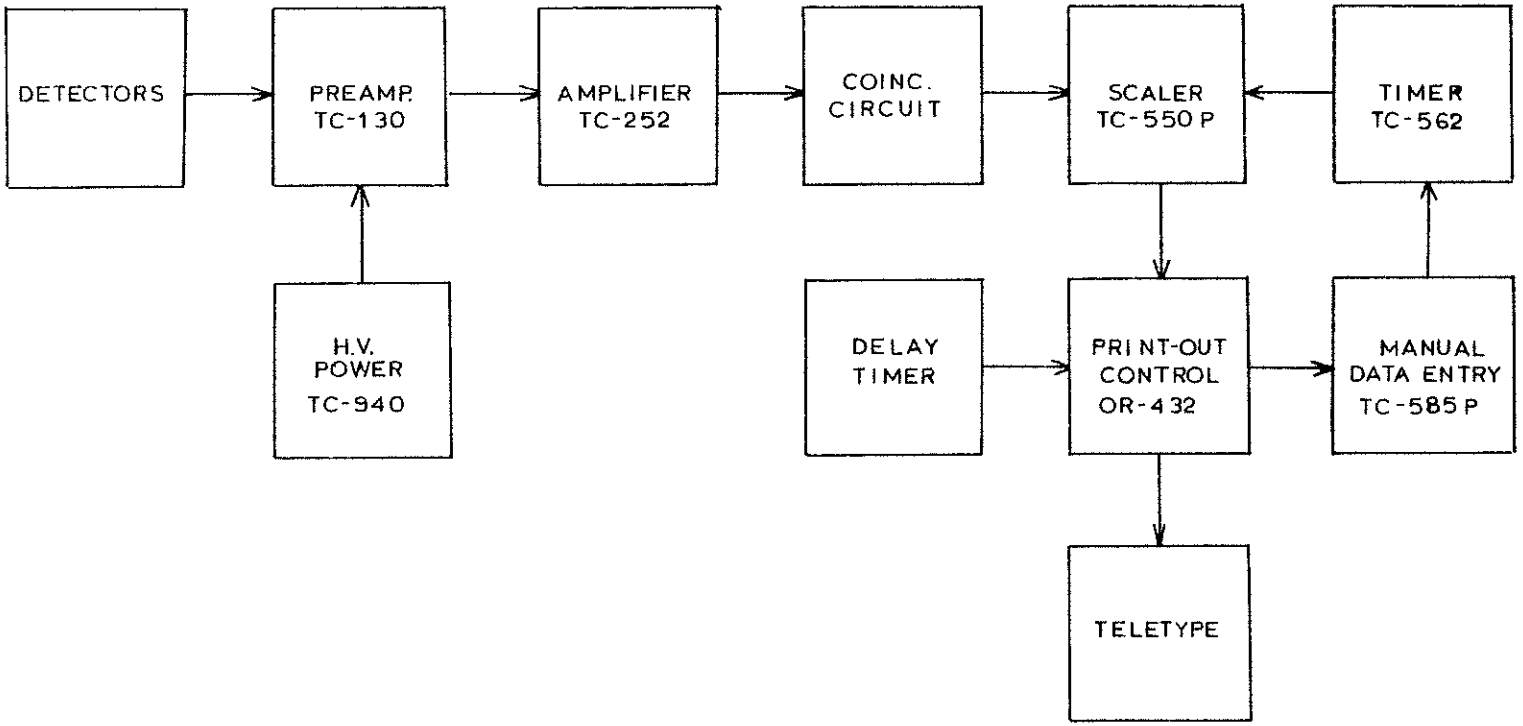

FIGURE 2. DELAYED NEUTRON COUNTING APPARATUS

RESULTS AND DISCUSSION

As the uranium-235 quantity in the sample approaches 200 mg, significant self-shadowing to the neutron flux occurs as shown in the calibration curve, Figure 3. At these levels, thorough mixing of the standards and samples to obtain homogeneity is important to ensure uniform self-absorption.

The proposed procedure was used to analyze synthetic uranium dioxide-thorium dioxide mixtures with known uranium concentrations, and samples of pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads. With the latter samples an estimation of accuracy was obtained by using the average of many wet chemical results obtained by several laboratories as the true value. The NDA results, shown in Table I, were calculated from the determined uranium-235 values on the basis of the known isotopic abundances. A positive bias of about 3% is in evidence. It is estimated that the lower limit of determination is about 20 mg of uranium-235.

TABLE I

THERMAL NEUTRON ANALYSIS OF URANIUM-THORIUM MIXTURES

Sample Type	Approximate Quantity of U Determined, mg	Number of Determinations, N	Accuracy[a,b] (Difference), %	Precision, (RSD), %
UO_2-ThO_2	310	30	+ 3.12	0.65
Riffled Fuel Beads	510	29	+ 2.98	0.53
Unriffled Fuel Beads	510	30	+ 2.66	1.02

a. $\text{Accuracy} = \left(\frac{\text{Determined Value}-\text{"True" Value}}{\text{"True" Value}}\right) \cdot 100$

b. "True" value obtained from 17 values in the case of the riffled beads, and 18 values on the unriffled.

Future work designed to reduce the effects of self-absorption will involve modification of the source configuration to increase the flux of neutrons of intermediate energy.

REFERENCE

1. Fabricated by the Department of Applied Science, Brookhaven National Laboratory, Upton, N. Y.

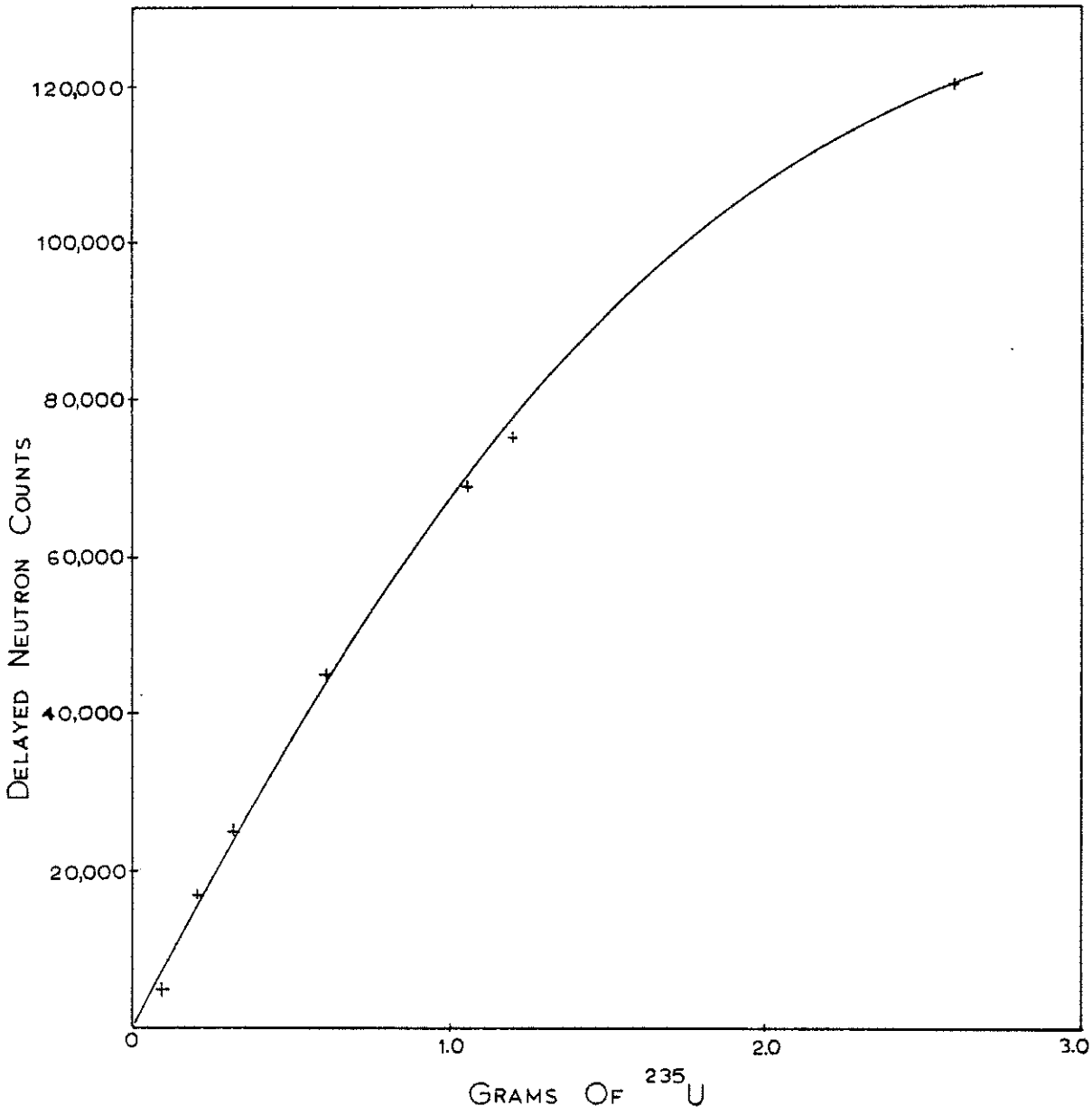

FIGURE 3. DELAYED NEUTRON CALIBRATION CURVE.

PREPARATION OF TEST MATERIALS FOR AN INTERLABORATORY CALIFORNIUM-252 ACTIVATION ANALYSIS EVALUATION PROGRAM

N. M. Trahey, J. M. Scarborough and L. Z. Bodnar

Investigations designed to evaluate the general applicability of californium-252 as a neutron source for activation analysis have been underway for several years within the Atomic Energy Commission. As part of this continued evaluation, Savannah River Operations Office (SROO) was given the responsibility of administering an interlaboratory evaluation program involving the use of californium-252 for activation analysis, and the New Brunswick Laboratory (NBL) was assigned the task of implementing the preparation and distribution of the test materials. The test materials were to consist of one 2N nitric acid solution containing 13 elements at various trace levels, and one solid material composed of a 70% silica, 20% iron oxide and 10% calcium carbonate matrix containing the identical trace elements at different concentration levels. The preparation and characterization of these test materials are described in the present report.

Part I. Preparation of Test Materials

It was requested of NBL that these test materials be prepared with the trace impurities at known concentrations within the definite concentration ranges listed in Table I.

TABLE I

SPECIFIED CONCENTRATION RANGES FOR TRACE ELEMENTS IN TEST MATERIALS

Element	Concentration Range, μg/g	Element	Concentration Range, μg/g
Na	100-1000	As	20-200
Al	50-500	Se	500-5000
V	10-100	Mo	400-4000
Mn	2-20	Cd	500-5000
Co	100-1000	Eu	0.2-2.0
Cu	20-200	Hg	300-3000
Zn	1000-10,000		

The test materials were to be essentially a dilute nitric acid solution for the liquid material, and a 70% silica, 20% iron oxide, and 10% calcium carbonate matrix for the solid material. Note that the concentrations were to be prepared and reported on a weight basis, μg/g of test material.

EXPERIMENTAL

Reagents and Apparatus

Silica, prepared from certified ACS reagent silicic acid, 325 mesh, by drying at 160°C for 48 hr and igniting at 500°C for 16 hr.

Ferric Oxide, certified ACS reagent.

Calcium Carbonate, certified ACS reagent.

All other reagents were either high-purity or analytical reagent-grade except as otherwise stated.

Water, deionized.

V-Blender, polymethylmethacrylate.

Ball Mill, polyethylene with porcelain balls.

Sieve, 40 mesh, nylon.

Procedure

Preparation of Stock Solutions

Prepare all stock solutions so that the concentration is known both by volume and by weight of final solution.

Sodium, 100.0 mg/ml and 81.71 mg/g. Prepare by dissolving $NaNO_3$ in water and diluting to volume and weight.

Aluminum, 20.0 mg/ml and 18.17 mg/g. Prepare by dissolving $Al(NO_3)_3 \cdot 9H_2O$ in water and diluting to volume and weight. Determine the final concentration by evaporating an aliquot, and igniting to Al_2O_3, and weighing.

Vanadium, 2.0 mg/ml and 2.00 mg/g. Prepare by dissolving NH_4VO_3 in water and diluting to volume and weight. Determine the final concentration by evaporating an aliquot, igniting to V_2O_5, and weighing.

Manganese, 10.0 mg/ml and 9.76 mg/g. Prepare by dissolving Mn metal in dilute HNO_3 and diluting to volume and weight.

Cobalt, 50.4 mg/ml and 44.66 mg/g. Prepare by dissolving Co metal in dilute HNO_3 and diluting to volume and weight.

Zinc, 50.0 mg/ml and 44.85 mg/g. Prepare by dissolving Zn metal in dilute HNO_3 and diluting to volume and weight.

Arsenic, 10.5 mg/ml and 10.34 mg/g. Prepare by dissolving As_2O_3 in 2% HNO_3 and diluting to volume and weight.

Selenium, 94.8 mg/ml and 89.65 mg/g. Prepare by dissolving H_2SeO_3 in dilute HNO_3 and diluting to volume and weight. Determine the final concentration by reducing an aliquot with hydroxylamine hydrochloride and weighing the selenium metal.

Molybdenum, 99.9 mg/ml and 89.00 mg/g. Prepare by dissolving $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in dilute NH_4OH and diluting to volume and weight. Determine the final concentration by evaporating an aliquot, igniting to MoO_3, and weighing.

Cadmium, 70.0 mg/ml and 62.89 mg/g. Prepare by dissolving Cd metal in dilute HNO_3 and diluting to volume and weight.

Mercury, 100.4 mg/ml and 88.70 mg/g. Prepare by dissolving Hg metal in dilute HNO_3 and diluting to volume and weight.

Copper, 10.2 mg/ml and 9.40 mg/g. Prepare by dissolving Cu metal in HNO_3 and diluting to volume and weight.

Europium, 1.00 mg/ml and 0.987 mg/g. Prepare by dissolving Eu_2O_3 in HNO_3 and diluting to volume and weight. Determine the final concentration by reducing an aliquot on a Jones reductor, adding the reduced aliquot to excess ferric chloride, and titrating the ferrous iron formed with potassium dichromate.

Preparation of Dilute Acid Test Material

Weigh a 9-kg quantity of 2N HNO_3 into a large carboy. Add weighed aliquots of the appropriate size of each stock solution. Mix thoroughly. Calculate the concentration of additives in µg/g of final solution. Determine a density value for the solution to obtain the concentrations on a volume basis. Bottle the test material in 1-l. glass bottles with polycone screw caps.

Preparation of SiO_2-Fe_2O_3-$CaCO_3$ Matrix Test Material

(NOTE! Perform most of these operations in a hood and wear a surgical mask and eye goggles because the finely divided materials dust badly.)

Weigh into a No. 13 porcelain evaporating dish 2800 g of silica. Weigh out appropriate aliquots of each trace element stock solution and combine all the trace element aliquots in 1.3 l. of 2N HNO_3 contained in a 2-l. separatory funnel except those for mercury, selenium and molybdenum. Add the mixed solution to the silica with constant mixing with a large plexiglass spatula. Rinse the separatory funnel with small amounts of 2N HNO_3 and add the rinsings to the dish with mixing. Add the mercury, selenium and molybdenum aliquots individually to the silica in the same way. Blend the mixture thoroughly and add water until the mixture changes from a lumpy paste to a smooth slurry. (The total volume of liquid required to obtain this creamy mixture is about 3350 ml.)

Place the dish in a drying oven at 110°C for 24 hr. Mix the cooled contents thoroughly and repeat the drying for 24 hr until the weight is constant (about 120 hr). Add 800 g of iron oxide and 400 g of calcium carbonate, mixing dry but thoroughly after each addition. Place the mixture in a V-blender and mix for 8 hr. Transfer the mixture to a ball mill and mill for 36 hr. Sieve the material through a 40-mesh nylon screen and return it to the V-blender for an additional 4 hr of blending. Bottle the test material in 2 polyethylene containers.

DISCUSSION OF PREPARATIONS

The nature of the solid matrix composition precluded the usual preparatory procedure of using standard pools of trace elements added to the premixed matrix because the dilute acid pools would destroy portions of the calcium carbonate and iron oxide. For this reason the pools had to be added to the silica and the acid removed before the calcium carbonate and iron oxide were added.

A single pool could not be made of all the trace element aliquots; mercury, selenium and molybdenum precipitated when added to the other elements. Accordingly, separate pools were made of these elements.

In the addition of the pools to the silica, the usual technique of adding the minimum amount of liquid just to wet the solid could not be used here. When this procedure was applied, the silica proved difficult to wet: large lumps together with dry powder were apparent until sufficient liquid was added to form the creamy slurry. Only this slurry could be blended efficiently.

For the solid test material, the aliquot weights and resulting calculated concentrations are given in Table II. These calculated concentrations will differ from the final concentrations if the "blank" matrix mixture contains traces of the particular element. In the case of manganese, no aliquot was added because analyses of the blank matrix materials indicated that the desired level would be obtained by the "blank" quantities only.

Homogeneity of the solid test material was verified by emission spectrographic analyses of random bottled samples for all elements except selenium, arsenic, sodium and europium.

Of some concern was the stability, that is, freedom from precipitation, of the liquid test material for at least a 6-month period. Already observed was the precipitation of $HgSeO_3$ in a dilute acid mixture. There was also some question about the stability of molybdate in the acid mixture. To select the proper acid concentrations for the test material, a series of solutions was prepared containing the elements in the described concentrations but with different amounts of HNO_3. When the trace element solution aliquots were added to water, hydrolysis of some of the elements occurred rapidly. When $1\underline{N}$ HNO_3 (or H_2SO_4) was used, precipitation in the solution become apparent in a matter of hours. However, when $2\underline{N}$ HNO_3 was used, the solution appeared to be completely free

of precipitation for at least 2 weeks. This concentration was used for the final master solution, aliquots of which are still free of any sediment after standing for 6 months.

TABLE II

WEIGHT OF STOCK SOLUTION ALIQUOTS TAKEN AND CALCULATED CONCENTRATION-SOLID TEST MATERIAL

Trace Element	Aliquot Used, g	Calculated Concentration, μg/g
Na	19.532	376
Al	88.717	380
V	158.76	75
Mn	--	0
Co	22.216	234
Cu	10.893	24
Zn	266.85	2820
As	15.074	37
Se	54.736	1156
Mo	127.50	2674
Cd	96.427	1429
Eu	5.0462	1.1
Hg	27.428	573

Weight of Final Mixture = 4244.4 g

The trace element solution aliquot weights and the final calculated concentrations for the liquid test material are given in Table III.

TABLE III

WEIGHT OF ALIQUOTS TAKEN AND CALCULATED CONCENTRATIONS-LIQUID TEST MATERIAL

Trace Element	Aliquot Used, g	Calculated Concentration, μg/g
Na	88.811	675
Al	220.33	372
V	99.751	18.5
Mn	5.2707	4.7
Co	33.774	140
Cu	106.60	93
Zn	223.28	931
As	73.845	71
Se	105.77	882
Mo	352.21	2914
Cd	398.01	2327
Eu	10.110	0.9
Hg	113.10	933

Weight of Final Mixture = 10,756 g

Density of Final Mixture = 1.0721 g/ml

Part II. Analysis of Test Materials

The final silica-iron oxide-calcium carbonate matrix and the 2N HNO_3 test materials were analyzed chiefly by spectrophotometric methods for the trace element concentrations. Additional data were provided by atomic absorption and flame emission spectrophotometry, emission spectrometry, spark source mass spectrometry and polarography.

EXPERIMENTAL

Reagents and Apparatus

The reagents used for each determination can be found in the reference for the particular method.

Spectrophotometer. Beckman Model DU.

Polarograph, Sargent Model XXI, used with a dropping mercury electrode.

Emission Spectrograph, Jarrell-Ash, 3.4 Ebert, and Jaco Varisource.

Spark Source Mass Spectrometer, Associated Electrical Industries MS-7 instrument modified for electrical detection by the manufacturer.

Atomic Absorption Spectrophotometer, Perkin-Elmer Model 403, with associated hollow-cathode lamps.

Procedure

Dissolution of Solid Test Material for Analysis

Transfer a 5-g sample of the solid test material to a 250-ml beaker and cover with a watch glass. Carefully add about 40 ml of 1:3 HNO_3:HCl into the beaker in small portions. When the reaction stops, rinse down the watch glass and beaker sides with about 5 ml additional acid mixture. Warm the solution on a steam bath for 1 hr and cool. Filter the mixture through Whatman No. 42 paper, washing the residue and paper thoroughly with water. Reserve the filtrate.

Transfer the residue and filter paper to a covered platinum dish. Ignite the paper. Dissolve the cooled residue by adding 10 to 15 ml HF and 1 ml of HNO_3. Evaporate the solution to near dryness. Dissolve the salts in 1 to 2 ml of HCl and a small amount of water and add the solution to the reserved filtrate. Dilute the solution to volume in a 500-ml volumetric flask.

Determination of Individual Trace Elements

Table IV lists the methods used for each trace element.

TABLE IV

METHODS USED FOR ANALYSES OF TEST MATERIALS

Trace Element	Reference	General Method[a]
Na	-	AAS (+F)
Al	1	SP with cupferron and oxine extraction
	-	AAS
V	1	SP with oxine extraction
	-	AAS
Mn	2	SP with periodate oxidation
	-	AAS
Co	1	SP with 1-nitroso-2-naphthol
	-	AAS
	3	P after dithizone separation
Zn	1	SP with dithizone extraction
	-	AAS
	3	P after dithizone separation
As	1	SP with distillation and molybdenum blue formation
	4	ES-boiler-cap technique
Se	1	SP with hydroxylamine and stannous chloride reductions
Mo	1	SP with thiocyanate
	-	AAS
Cd	1	SP with dithizone extraction
	-	AAS
	3	P after dithizone separation
Eu	-	SSMS
Hg	1	SP with dithizone extraction
	4	ES-boiler-cap technique
Cu	5	SP with neocuproine extraction
	-	AAS
	3	P after dithizone extraction

a. F = flame photometry
SP = spectrophotometry
AAS = atomic absorption spectrophotometry
P = polarography
SSMS = spark source mass spectrometry
ES = emission spectrometry

Except for a few modifications made chiefly to eliminate the effect of the large amounts of iron in the prepared solution of the solid test material, the details of each procedure are essentially as described in the particular reference. Briefly, these modifications include (1) extending the detection limits for manganese by decreasing the volume of the final solution to be measured; (2) increasing the cupferron concentration and extraction time for the more complete removal of iron in the aluminum determination; (3) prior precipitation of selenium with hydroxylamine hydrochloride before the usual procedure is applied with stannous chloride. Other minor modifications were made in several procedures.

All spectrophotometric determinations were made only after the effectiveness of the proposed unmodified or modified procedure was verified by the analysis of standards containing the same ratio of iron(III) to impurity expected in the prepared solution of the solid test material. The same procedures were used to analyze both the solid test material and the liquid test solutions.

Atomic absorption spectrophotometric determinations were also made for most elements in both test materials. Polarography was used to gain additional data for cobalt, copper, zinc and cadmium in the solid mixture. No other elements could be conveniently determined by the technique. Atomic absorption and flame emission spectrophotometry was relied upon exclusively for the Na values, and spark source mass spectrometry was likewise relied upon for the Eu level in the solid.

To obtain at least an approximate calculated value for the levels in the solid test material it was necessary to determine the blank levels in the silica, iron oxide and calcium carbonate matrix components. These determinations were made by emission spectrometry, and by atomic absorption and flame emission spectrophotometry with the results shown in Table V.

TABLE V

"BLANK" LEVELS IN THE MATRIX COMPONENTS

	Concentration, μg/g			
Trace Element	SiO_2	Fe_2O_3	$CaCO_3$	Total[a]
Na	--	--	--	110[b]
Al	70	10	5	85
Zn	--	20	--	20
Mo	<10	8	--	13
Cu	<10	<10	--	10
Mn	--	100-120	--	110

a. For a "less-than" value the amount present is arbitrarily assumed to be one-half of the value given.

b. Determined only in the mixture by atomic absorption and flame emission spectrophotometry; all other values determined by emission spectrometry.

In Table VI are given the concentrations of trace elements added plus the concentration originally present (blank values) together with the levels found by analysis. Also given are the assigned levels for each element. These assigned values are the most reasonable levels to which the activation analyses should be compared, and they were obtained by the following considerations. The spectrophotometric and polarographic determinations are presumed to be accurate within $\pm 5\%$; the atomic absorption and flame emission spectrophotometric determinations should be within 10%, and the emission spectrographic values should be within 25%. In every case except for selenium, aluminum and copper chiefly in the solid test material, the spectrophotometric results are within 5% of the "made-up" value. Therefore, for all but these elements (and sodium for which no spectrophotometric determinations were run) the assigned value is a rounded "made-up" value. Most of the analyses thus can be considered to be confirmatory in nature. When the analyses were relied upon, the spectrophotometric results were considered to be the more reliable. The selenium analytical results apparently reflect some losses from volatilization during the preparation of the solid test material. At any rate, for this element the assigned values are based upon the analyses. Likewise, the assigned sodium values are based upon the analyses for two reasons: (1) there are apparently small "blank" quantities added in the reagents; (2) the blending operation for the solid test material undoubtedly added some sodium. It was felt that the ball-milling also added some aluminum, the assigned values for which are also based upon the analysis in the solid test material. For the copper value of the solid test material, the good reliability of the spectrophotometric procedure and the uncertainty of the added "blank" quantity both made the rounded analytical value the most reasonable value.

Table VII gives the added and found quantities for the liquid test material together with the rounded assigned values.

TABLE VI

TRACE ELEMENT CONCENTRATIONS IN SOLID TEST MATERIAL

Trace Element	Concentration, μg/g							
	Calculated			Found				
	Added	"Blank"	Total	SP	AAS	P	SSMS	Assigned
Na	376	110	486	--	570[a]	--	--	570
Al	380	85	465	494	420	--	--	490
V	75	5	80	82	78	--	--	80
Mn	0	110	110	107	83	--	--	110
Co	234	--	234	227	193	250	--	230
Cu	24	10	34	31	28	--	--	30
Zn	2820	20	2840	2847	--	2897	--	2840
As	37	--	37	34	50[b]	--	--	35
Se	1156	--	1156	1022	--	--	--	1020
Mo	2674	13	2687	2721	2850	--	--	2690
Cd	1429	--	1429	1411	1348	1448	--	1430
Eu	1.1	--	1.1	--	--	--	1	1.1
Hg	573	--	573	558	670[b]	--	--	570

a. By atomic absorption and flame emission spectrophotometry

b. By emission spectrometry.

TABLE VII

TRACE ELEMENT CONCENTRATIONS IN LIQUID TEST MATERIAL

Trace Element	Concentration, μg/g			
		Found		
	Added	SP	AAS	Assigned
Na	675	--	688[a]	690
Al	372	352	364	370
V	18.5	18.7	22	20
Mn	4.7	4.0	4.3	5
Co	140	135	132	140
Cu	93	92	92	95
Zn	931	929	895	930
As	71	69	--	70
Se	882	839	--	840
Mo	2914	2892	2425	2910
Cd	2327	2276	2122	2330
Eu	0.9	--	--	0.9
Hg	933	945	--	930

a. By atomic absorption and flame emission spectrophotometry.

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ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF MERCURY IN TEST MATERIALS FOR THE CALIFORNIUM-252 EVALUATION PROGRAM

R. L. Graff

The two synthetic test materials prepared at the New Brunswick Laboratory (NBL)[1] for the interlaboratory californium-252 activation analysis evaluation program consisted of a 2N nitric acid solution and a 70% silica, 20% iron oxide, 10% calcium carbonate matrix, both containing 13 trace elements at various levels. Mercury, at a level of 300 to 3000 ppm, was one of these trace elements.

These test materials, after preparation, were analyzed for the trace elements chiefly by spectrophotometric methods.[1] Mercury was determined by a conventional dithizone procedure,[1] and also by an emission spectrometric procedure.[2] When atomic absorption spectrophotometry was attempted for mercury, extremely high and erratic results were unexpectedly obtained. It is believed that these anomalous results were caused by differences in the valence state of mercury in the sample and standards.

EXPERIMENTAL

Reagents and Apparatus

HNO_3 and HCl, redistilled from quartz.

HF, redistilled from platinum.

Mercuric Oxide and Mercuric Chloride, reagent grade.

Atomic Absorption Spectrophotometer, Perkin-Elmer Model 403, equipped with air-acetylene burner head, mercury hollow-cathode lamp, and Deuterium Arc Background Corrector.

Procedure

Preparation of Standard Solution. Prepare two stock solutions: one from HgO dissolved in HNO_3; one from $HgCl_2$ dissolved in water. Dilute both solutions with 2N HNO_3 to the appropriate volume to obtain solutions containing 5 mg/ml. Dilute these stock solutions with 2N HNO_3 to obtain two series of standards containing from 5 to 500 μg/ml.

Prepare a third and fourth series of standards by spiking solutions of the "blank" matrix material containing iron and calcium salts. Dissolve the blank matrix material as described below under Analysis.

Analysis

2N HNO_3 Test Material. Dilute this solution with 2N HNO_3 to various levels to ensure that the measurements fall within the optimum instrumental range: 1:5 up to 1:200.

Solid Matrix Test Material. After dissolution in HCl, treatment with HF to remove silica, and several evaporations with HNO_3 to remove chlorides and fluorides, dilute to 100 ml with 2N HNO_3. Prepare dilutions with 2N HNO_3 as above.

Carry out the atomic absorption spectrophotometric measurements using the Hg line at 2536 Å on standards and samples according to the general procedure outlined in the Perkin-Elmer manual.[3]

RESULTS AND DISCUSSION

The results obtained on the liquid test solution using standards prepared by dissolving HgO in HNO_3, were much higher than the quantities originally added, and were also higher than those obtained by the dithizone spectrophotometric procedure. The use of the standards prepared from $HgCl_2$ gave essentially the same high results. Determination of mercury in the solid test material by comparison to similar standards also gave higher results than the "added" values. These results were also higher than those obtained both by emission spectrometry[2] and spectrophotometry after dithizone extraction.[1] Measurements made with and without the background corrector were essentially identical. The averaged results are shown in Table I.

TABLE I

ATOMIC ABSORPTION SPECTROPHOTOMETRIC RESULTS ON TEST MATERIALS COMPARED TO "ADDED" VALUES AND RESULTS BY OTHER METHODS

	Mercury, μg/g	
Method	2N HNO_3 Test Material	Solid Matrix Test Material
Atomic Absorption	1870	800
Emission Spectrometry	--	670
Dithizone Extraction	945	558
"Added"	933	573

Since cobalt is present as one of the trace elements in the test materials and is known to interfere with the mercury determination, cobalt was added to standard solutions in the same concentrations as are present in the test materials. No significant effect on the mercury measurements was noted.

Four test solutions were prepared by dissolving mercury metal in HNO_3 and diluting to volume with 2N HNO_3 to serve as "knowns". In dissolving the mercury for these solutions, three were dissolved by the gradual addition of a minimum of HNO_3, one was dissolved in a large excess of HNO_3 added at one time. Only in the

case of the latter solution was the correct result obtained; results with the other three solutions were again very high.

In the Perkin-Elmer manual,[3] the possibility of enhancement of the mercury absorbance by mercury(I) is noted. Qualitative tests for mercury(I) involving precipitation of insoluble mercurous chloride were then made on the various solutions. Mercury(I) was found to be present in appreciable quantity in the 2N HNO_3 test material and in the three control "knowns" discussed above. A small amount appeared to be present in the solutions prepared from the solid matrix test material. No mercury(I) could be detected in the fourth control "known" which had been found to behave correctly. No mercury(I) was found in the 2N HNO_3 standard solutions prepared from HgO and $HgCl_2$.

Apparently, then, the high results obtained in this work are due to the presence of mercury(I) in the sample solutions. In preparing a mercury solution by dissolving the metal in HNO_3 some mercury(I) can be formed as shown by its presence in the three control "known" solutions. The mercury that was added to the two californium-252 test materials was prepared in this manner. Moreover, once mercury(I) is present, even in 2N HNO_3, it appears to remain unchanged for long periods of time. Atomic absorption spectrophotometric measurements made 6 weeks after preparing the 2N HNO_3 test material still gave the abnormally high results.

Thus, in the determination of mercury by atomic absorption spectrophotometry as in chemical methods, it is essential that the element be converted to a known oxidation state.

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DETERMINATION OF THORIUM IN URANIUM-THORIUM MIXTURES

J. M. Scarborough

Little specific information is available on the determination of thorium in pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads. Recently, an ethylenediaminetetraacetic (EDTA) titration of the thorium after separation from the uranium on a strongly basic ion-exchange resin column was reported.[1] Apparently in many cases the conventional gravimetric procedure involving ammonia, fluoride and oxalate precipitations is being used. This method is lengthy and tedious.

In the present work, a direct EDTA titration was studied. The proposed method was assessed by the analyses of synthetic uranium dioxide-thorium dioxide mixtures. The thorium dioxide used for these mixtures was first carefully characterized for assay by three techniques: EDTA titration, oxalate precipitation and ignition to oxide, and direct ignition plus emission spectrographic determination of impurities for a gravimetric correction. The results obtained by the EDTA titrimetric determination of thorium in the mixed oxides were then compared to those obtained by the conventional gravimetric method.

EXPERIMENTAL

Reagents and Apparatus

EDTA Titrant, 0.01M, prepared by dissolving 7.4 g of disodium ethylenediaminetetraacetate in 2 l. of water.

Standard Copper Solution, 1.3 mg/g, prepared by dissolving Cu metal (99.999% pure) in HNO_3 and diluting to weight.

Acetate Buffer, pH 6.0, prepared by adding 28 g. of sodium acetate trihydrate to about 1 l. of water and adjusting the pH to 6.0 with acetic acid.

Potassium Acid Phthalate Buffer, pH 2.5, prepared by mixing 500 ml of 0.1M potassium acid phthalate with 388 ml of 0.1N HCl.

Xylenol Orange (XO), 0.1% in ethyl alcohol.

1-(-2 Pyridylazo)-2-Naphthol (PAN), 0.1% in ethyl alcohol.

Thorium Dioxide, high-purity

Uranium Dioxide, reactor-grade.

Procedures

Standardization of EDTA

Standardize the EDTA against copper as described in reference (2) noting that the color of the PAN end point appears to be green rather than yellow as reported by the authors.

Preparation of Thorium Solution

Dissolve a 2.5 g sample of thorium dioxide or an equivalent weight of thorium dioxide-uranium dioxide in HNO_3 containing a drop of HF by warming the mixture until dissolution is complete. Dilute to a known weight of solution.

Titrimetric Determination of Thorium with EDTA

Place a weighed aliquot of the solution to contain about 0.1 g of thorium in a 250-ml beaker and evaporate to dryness on a steam bath. Cool the residue, and add with stirring 75 ml of potassium acid phthalate buffer, pH 2.5. Add 6 drops of XO indicator, and titrate to the disappearance of the pink tint of the Th-XO complex. (Good lighting and a white background are necessary to see the color change.)

Gravimetric Determination of Thorium with Oxalate

Evaporate a weighed aliquot of the nitric acid solution containing about 0.3 g of thorium on a steam bath. Add 5 to 10 ml of water and again evaporate to dryness. Dissolve the residue in 5 ml of water and add 25 ml of 10% oxalic acid solution. Heat the mixture to 80°C for 1.5 hr, and then allow the precipitate to digest overnight at room temperature.

Filter the precipitate through Whatman No. 42 paper, washing the paper and precipitate well with 1% oxalic acid solution. Ignite the paper and precipitate in a platinum crucible at 400°C for 1 hr, then at 1100°C to constant weight (about 3 hr), and weigh.

Gravimetric Determination of Thorium in Thorium Dioxide by Direct Ignition

Place a weighed 2.5 g sample in a platinum crucible. Ignite at 1100°C to constant weight. Determine the impurities present by emission spectrometry using the carrier distillation technique. Correct the assay value for the concentration of metallic impurities present.

RESULTS AND DISCUSSION

Ten samples of the same thorium dioxide were analyzed by the EDTA titration and by the gravimetric (oxalate) procedure. Three samples of the thorium dioxide were also analyzed by the direct ignition procedure, Table I. The emission spectrometric values for the impurities are shown in Table II.

TABLE I

DETERMINATION OF THORIUM IN THORIUM DIOXIDE

	Thorium, g Th/g ThO_2		
	EDTA	Oxalate	Direct Ignition[b]
	0.8758	0.8762	0.8766
RSD,[a] %	0.03	0.04	0.007

a. Relative standard deviation

b. An average value for the impurity elements of 600 μg/g was used.

TABLE II

IMPURITIES IN ThO_2 OBTAINED BY EMISSION SPECTROMETRY

Element	Concentration, μg/g Th	Element	Concentration, μg/g Th
Ag	50	Mg	0.5
Al	5	Mn	0.5
B	0.2	Mo	< 1
Bi	0.2	Ni	2
Ca	2	Pb	5
Cd	< 0.1	Si	500
Co	< 1	Sn	< 1
Cr	2	V	< 10
Cu	0.2	Zn	< 10
Fe	15	Total a	600 ± 200

The averages of the results for the three methods of determining the thorium concentration in the thorium dioxide agree fairly well and have an overall average value of 0.8762 g Th/g ThO_2 with a weighted standard deviation of 0.0000558 g Th/g ThO_2 (0.015% relative). These estimates were obtained as follows:

$$\text{overall average} = \bar{\bar{X}} = \frac{\Sigma \bar{X}_i}{\text{number of averages}}$$

$$\text{variance } (\bar{\bar{x}}) = s^2_{\bar{\bar{x}}} = \frac{1}{(\text{number of averages})^2} \cdot \Sigma_i (\text{variance } \bar{x}_i)$$

$$= \frac{1}{(\text{number of averages})^2} \cdot \left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2} + \frac{s_3^2}{n_3} \right)$$

The average assay value is calculated to be 99.70% thorium dioxide.

The EDTA titration was applied to a series of 10 thorium dioxide-uranium dioxide mixtures containing a fixed Th:U ratio and prepared from the same thorium dioxide as was analyzed above. These results are shown in Table III. Three additional mixtures containing variable Th:U ratios were then analyzed, with 3 determinations being made on 3 aliquots of the solution prepared from each mixture.

TABLE III

EDTA TITRATION OF THORIUM IN THORIUM-URANIUM MIXTURES

Th:U Ratio	N	Thorium, g/g ThO_2	RSD, %
25	10	0.8760	0.08
10	3	0.8769	0.02
16	3	0.8750	0.06
25	3	0.8763	0.01

These results were then compared to the results obtained[3] by analyzing in triplicate 6 samples of thorium dioxide-uranium dioxide mixtures by the conventional gravimetric method involving ammonia, fluoride and oxalate precipitation followed by ignition to thorium dioxide, Table IV.

TABLE IV

COMPARISON OF RESULTS OBTAINED BY EDTA TITRATION AND CONVENTIONAL GRAVIMETRIC METHOD

Average	(N)	EDTA	(N)	Gravimetric
Assay, gTh/g ThO_2	(19)	0.8759	(18)	0.8754
RSD, %		0.08		0.44
Bias, gTh/g ThO_2 [a]		-0.0003		-0.0008

a. Absolute difference between assigned value and determined value.

The data in Tables III and IV are expressed as thorium assay values calculated from the known weights of thorium dioxide and uranium dioxide in the mixtures.

It can be seen that the direct EDTA titration appears to be superior to the conventional gravimetric procedure for the analysis of mixtures of thorium and uranium. A future report will be made of the results obtained by using the EDTA titration and the conventional gravimetric procedure for the analysis of graphite- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads.

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DISSOLUTION OF PYROCARBON- AND SILICON CARBIDE-COATED URANIUM-THORIUM CARBIDE FUEL BEADS — CHLORINATION AND FUSION DISSOLUTIONS

C. E. Hedrick

Pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads are difficult to dissolve for chemical analysis because of the refractory nature of the coatings. At the New Brunswick Laboratory (NBL), the beads are routinely dissolved by tedious and time-consuming fusions, first with sodium carbonate and then with sodium bisulfate.[1]

Previous work[2] at NBL has been directed at speeding up the fusion dissolution of the beads. Fusions with many salts and salt mixtures were tested in a variety of crucibles. On the basis of speed of dissolution, absence of reactivity towards platinum and other crucibles, freedom from reaction gassing, ease of work-up after fusion, and compatibility of the final solution with the NBL titrimetric method for determining uranium, the best mixture found at that time was (10+1) sodium carbonate plus sodium chromate mixture. Yet this technique has shortcomings: in the work-up of the melt, a large amount of insoluble chromium sulfate is obtained unless perchloric acid is used as the solubilizing acid. Moreover, the large quantity of chromium present in the final solution causes difficulties in the titrimetric method.

In the present work, the fusion studies were continued. The tests involved the use of only small quantities of sodium chromate or sodium vanadate added to the sodium carbonate. In addition, the high-temperature chlorination method reported by Robertson[3] was investigated. Certain modifications in this technique were found to be necessary.

Fusion Studies

EXPERIMENTAL

All reagents are analytical reagent-grade unless otherwise stated.

Quartz Tubing, 25 cm long by 7 mm OD.

Blast Burner

Tank Oxygen, USP.

Procedure

Weigh a 5-g sample of fuel beads into a 125-ml platinum dish. Cover the dish loosely and ignite for 1 hr with a blast burner while directing a stream of oxygen into the dish with the quartz tubing. Cool the dish, add 5 g of sodium carbonate and 50 mg of sodium vanadate or sodium chromate. Again ignite as above for 1 hr. Cool the dish, add 10 g additional sodium carbonate, and ignite for 2 hr as before. Cool the dish.

Add in small quantities, washing the cover and dish sides down when necessary, about 40 ml of 8M H_2SO_4 and 40 ml HF. Replace the cover and digest for 1 hr at low heat on a hot plate. Remove the cover, wash it down with water, increase the temperature of the hot plate and evaporate the solution to fumes. Add H_2SO_4, if necessary, to complete the removal of fluoride. Fume at high heat until the mass nearly solidifies. Add 20 g of sodium bisulfate and fuse strongly until the melt is clear. Cool the melt and dissolve the cake in water. If a small residue remains, filter the solution through Whatman No. 41 paper reserving the filtrate. Dry the paper in a platinum crucible, ignite, and fuse the residue with 100 mg of sodium nitrate plus 3 g of sodium carbonate. Dissolve the fusion cake in 20 ml of (1+1) HNO_3 and add the solution to the reserved filtrate.

RESULTS AND DISCUSSION

Small amounts of sodium vanadate or sodium chromate appear to accelerate the fusion attack of the sodium carbonate to a significant extent. In addition, these quantities of vanadium or chromium in the final solution do not affect the NBL titrimetric method of determining uranium. With a sample-to-fusion mixture of (1:3), the silicon carbide coating in a 5-g sample is removed and about 80% of the core material is dissolved within 3 hr. The remaining core material is dissolved in the subsequent steps.

Unfortunately the vanadate or chromate accelerators in the carbonate fusion cause increased erosion of the platinum dishes. About 20 mg of platinum is lost with the vanadate mixture, about 9 mg with the chromate. Furnace fusions, or the use of sodium metaphosphate, which was also found to be a good activator, causes even greater losses of platinum. These platinum losses make the procedure somewhat more expensive and may necessitate an additional separation step in the titrimetric procedure in which platinum can interfere. The studies are continuing.

High-Temperature Chlorination

EXPERIMENTAL

Reagents and Apparatus

All reagents are reagent grade unless otherwise stated.

Chlorine, high-purity, with monel valve.

Activated Charcoal, 6 to 14 mesh.

Teflon Tubing, 6 mm OD with 1 mm wall thickness, for attachment to the chlorine tank valve.

Tygon Tubing. 1 cm ID with 2 mm wall thickness.

Quartz Wool, coarse.

Quartz Combustion Tube, 1 cm OD, 1 mm wall thickness, 77 mm long with constriction to 3 mm ID at 52 cm. The "short" end of the tube is the exit end.

Tube Furnace, horizontal, high temperature, with quartz liners, 36 mm OD, 2-mm wall thickness, and 60 cm long.

Procedure

Fit a loose plug of quartz wool in the longer end of the constricted quartz tube so that it fits snugly against the constriction. Add a weighed 15-g sample of beads to the tube held vertically and then fit another loose quartz plug about 1 cm above the sample charge so that the beads are held but are not tightly packed. Place the tube in the tube furnace at 900 to 1000°C and pass a stream of air at a flow rate of about 300 ml/min for 2 hr through the tube by means of tygon tubing fitted onto the "long" end of the tube. Cool the furnace to 600°C, remove the tube, and cool it to room temperature.

Pack the exit end of the tube with a 15-cm length of activated charcoal held in place again with quartz wool plugs. Insert the tube into the furnace, and while readjusting the furnace temperature to 1000°C, begin passing the chlorine, by means of a fresh piece of tubing fitted over the entrance end of the quartz tube, through the sample at a flow rate of 300 to 500 ml/min. When a temperature of 1000°C is reached, continue the chlorination for 45 min. Turn off the furnace, and when the temperature reaches 800°C, stop the chlorine flow. Remove the quartz tube and cool it to room temperature.

Remove the exit end quartz wool plug and place it in a 125-ml platinum dish. Pour the charcoal into the dish. Remove the second wool plug and add it to the dish. Hold the tube vertically over the dish (inlet end downward) and pour a small amount of methanol into the exit end to wet the sample charge. Now holding the tube near horizontal with the inlet end over the dish, transfer the charge plugs and residue to the dish by means of methanol. Dry the tube, and draw by suction about 25 ml of 1:1 HNO_3 into the exit end to remove U/Th chlorides, reserving the acid to be added to the solution of the oxidized cores.

Evaporate the methanol from the dish, apply a loose platinum cover, and ignite overnight in a muffle furnace at 900°C. To the cooled dish add 20 ml of HNO_3 and 20 ml of HF. Evaporate the mixture to dryness. Add 50 g of sodium bisulfate and fuse the oxides. Dissolve the cooled melt in water. If a small amount of residue remains, treat it by the sodium carbonate-sodium nitrate fusion described above under Fusion Procedure. Combine the 1:1 HNO_3 from the combustion tube wash and the residue solution with the solution of the oxides.

RESULTS AND DISCUSSION

Robertson[3] found that the most effective chlorination was obtained with a vertical tube containing the beads resting on a frit. Los Alamos Scientific Laboratory (LASL) has reported[4] a similar procedure. In the present work, the more convenient horizontal tube position was found to be effective for the oxidation and chlorination step provided that the beads are loosely packed and the gas flow rate is ample but low enough to prevent tight packing of the beads.

Robertson makes no mention of uranium losses during chlorination. In preliminary evaluation tests of the chlorination, it was found that appreciable amounts, 0.1 to 0.2%, of uranium (and quantities of thorium) volatilized from the charge material along with the silicon chloride and were lost. Initially, 2 U-tube traps in series immersed in ice-water were used to condense the silicon chloride and uranium/thorium; water traps were inconvenient because of the formation of silica gel. The cold U-tube traps hold all the uranium as shown by the absence of uranium in a third trap. When the charcoal column is used, no uranium is found in these two traps. Therefore, the U-tubes were eliminated. In Table I are given the results of three determinations of the uranium content of the identical sample of fuel beads as was used in an interlaboratory evaluation program[5] involving both chemical and non-destructive assays. The solutions prepared from each vial by the dissolution procedure were analyzed in triplicate. These values are comparable to those obtained in the interlaboratory study and indicate that the uranium recovery was complete.

TABLE I

RESULTS OBTAINED BY HIGH-TEMPERATURE CHLORINATION DISSOLUTION

Vial No.	Uranium, g/Vial	Average, g/Vial	Average, g/g
1	0.50326, 0.50304, 0.50355	0.50328	0.03331
2	0.50283, 0.50339, 0.50321	0.50314	0.03316
3	0.50880, 0.50880, 0.50862	0.50874	0.03328

Repeated attempts to completely dissolve the core material remaining after the chlorination by HNO_3-HF mixtures were invariably unsuccessful. Accordingly, the bisulfate fusion had to be used. The chlorination studies are continuing.

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SUMMARY OF AN INTERLABORATORY COMPARISON PROGRAM ON THE ANALYSIS OF PYROCARBON- AND SILICON CARBIDE-COATED URANIUM-THORIUM CARBIDE BEADS

C. D. Bingham and J. Whichard

In response to a request from a licensee and concurred in by the Directorate of Regulatoratory Standards, the New Brunswick Laboratory (NBL) sponsored an interlaboratory comparison program on the analysis of pyrocarbon- and silicon carbide-coated uranium-thorium carbide nuclear fuel beads. This material is manufactured during the production of High Temperature Gas-Cooled Reactor (HTGR) fuel.

A series of mixtures of urania (UO_2) and thoria (ThO_2) was prepared from characterized starting materials to serve as "knowns" by which to measure the accuracy of uranium and thorium determinations by each participating laboratory. Samples of beads from a single production lot were prepared in sealed glass vials. All of the (90) samples were assayed for uranium by non-destructive assay (NDA) techniques by each of three participating laboratories. Three oxide samples and six bead samples were sent to each of seven participating laboratories for destructive chemical assay of uranium and thorium.

A detailed description of the program, of the results and conclusions is contained in a separate report[1]. NDA data from the oxide samples reveal an apparent strong matrix effect in relating the responses of the oxide samples to those of standards prepared in each NDA laboratory. Two of the three NDA laboratories exceeded the prepared value by more than 2% (relative). With the exception of one laboratory, whose uranium data were consistently higher than those from other laboratories, the data from the chemical analysis of the oxide samples for uranium revealed a spread of $\pm 0.2\%$ (relative) about the prepared value. Uranium results on the bead samples from the same chemistry laboratories exhibited a spread of $\pm 0.9\%$ (relative) about the interlaboratory average. This increased spread could be attributed to variations within the uranium content of the bead population but more likely it reflects differences due to the effect of methods by which the participants solubilized the sample prior to analysis. Results from two of the three NDA laboratories fell within the range of the chemical data for the bead samples.

A Phase II program is being planned to define more clearly the state-of-the-art of the chemical analysis of these coated beads, and those parameters which adversely affect the overall reliability of the uranium measurement.

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MASS SPECTROMETRIC ISOTOPE DILUTION DETERMINATION OF URANIUM AND PLUTONIUM — VOLUMETRIC vs GRAVIMETRIC TECHNIQUES FOR PREPARING THE ISOTOPE MIXTURES

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

Mass spectrometric isotope dilution is used frequently at the New Brunswick Laboratory (NBL) for the determination of low levels of uranium and plutonium. In previous reports,[1,2] the procedures were described and precisions and accuracies were evaluated based upon volume additions of tracer and standard solutions. In the present work, both plutonium and uranium tracer solutions were assayed, and the precisions of the results obtained both by volumetric and gravimetric techniques for preparing the standard-tracer mixtures were compared.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus are as described previously[1,2] with the following exceptions:

Plutonium-242 Tracer Solution. Sufficient plutonium-242 as oxide is weighed and dissolved, and the resulting solution diluted to give solutions with a plutonium-242 concentration of about 6.1 μg/ml (4.5 μg/g) and 10.8 μg/ml (7.9 μg/g).

Total Plutonium Standard Solutions. Two solutions were prepared from National Bureau of Standards (NBS) SRM 949C plutonium metal to contain 11.06 μg/ml (8.07 μg/g) and 9.95 μg/ml (7.26 μg/g) of total plutonium.

Uranium-233 Tracer Solution. A solution containing about 0.94 mg/ml (0.75 mg/g) of uranium-233 was prepared from U_3O_8 made from uranium-233.

Total Uranium Standard Solution. A solution containing 0.74 mg/ml (0.72 mg/g) total uranium was prepared from NBS SRM 960 (NBL C8583) normal uranium metal.

Micropipets. Conventional micropipets consisting of syringe and removal tip were identified by number and calibrated, and were used only for one particular solution to prevent cross-contamination.

Procedure

Determine the concentration of plutonium and uranium in the tracers in separate analyses. Prepare the tracer-standard mixtures

by pipetting volume aliquots. Weigh the volumes used on a semi-microbalance to obtain the weights of the aliquots. Obtain the mass spectrometric measurements in the usual manner.[1,2] Repeat the assays over a period of months.

RESULTS AND DISCUSSION

The tracer solutions could not be prepared to accurately known concentrations because the tracer oxides used could not be sufficiently characterized for purity and stoichiometry. Estimations of accuracy, therefore, could not be obtained from the determined assay values.

The tracer was assayed by obtaining the mass spectrometric measurements, over a period of time, on a single standard-tracer mixture and calculating the tracer concentration on the basis of either the volumes or weights involved in the mixture. This procedure eliminated any difference in the results associated with the mass spectrometric measurements and allowed a strict comparison of the precision of each technique to be made. The data accumulated over a 9-month period are shown in Table I for plutonium-242 and in Table II for uranium-233. Although the weight aliquot technique appears to be slightly more precise, the relative standard deviations (RSD) in each case are not statistically different. Moreover, the precisions do not appear to be affected by the tracer concentration involved.

This study indicates that the preparation of tracer-standard mixtures for isotopic dilution assay by the use of volumes delivered by calibrated micropipets is essentially as precise as that by weight delivery.

TABLE I

PRECISION OBTAINED USING WEIGHT AND VOLUME ALIQUOTS: PLUTONIUM

Plutonium-242

µg/g				µg/ml			
Standard	Tracer	N	^{242}Pu Assay, RSD, %	Standard	Tracer	N	^{242}Pu Assay, RSD, %
8.065	4.486	4	0.41	11.057	6.150	4	0.43
7.257	4.470	3	0.15	9.947	6.124	3	0.17
8.065	7.885	10	0.15	11.057	10.802	10	0.16
8.065	7.898	5	0.33	11.057	10.812	5	0.30

TABLE II

PRECISION OBTAINED USING WEIGHT AND VOLUME ALIQUOTS: URANIUM

Uranium-233

mg/g				mg/ml			
Standard	Tracer	N	^{233}U Assay, RSD, %	Standard	Tracer	N	^{233}U Assay, RSD, %
0.7157	0.7525	6	0.32	0.7445	0.9441	6	0.34

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A FOCAL PROGRAMMING SYSTEM FOR AN ISOTOPE RATIO MASS SPECTROMETER LABORATORY*

L. C. Nelson, Jr.

The mass spectrometer installation at the New Brunswick Laboratory (NBL) has been operated under the control of a 4K PDP-8 computer for several years.[1,2] The application program, as written in assembly language, together with the floating point program, occupied 22 pages of core, was inefficiently written and was cumbersome to modify. Conversion to a FOCAL operating system was adopted in order to provide more efficient and flexible use of the computer system and hands-on operation by the mass spectrometer operators. To facilitate this change, special external functions for the operation of the analog-digital converter (ADC), the buffer-relay driver, and the real-time clock were written, and suitable functions to permit storing variables and chaining programs to and from a DF-32 disk were incorporated as additional FOCAL functions in the operating system.[3]

The ADC function (FADC) is written to process two arguments: one to specify the multiplexor channel; and one to determine the number of A/D conversions to be performed. All conversions resulting from a given command are summed and added to the floating accumulator for further processing. The real-time clock function (FCLK) is utilized to "slow down" the data-taking and to provide smoothed data since the mass spectrometer amplifiers, from which the signals are received, are comparatively sluggish in operation. The clock function also is used to provide settling time for the mass spectrometer magnet supply and the amplifier from which the data are derived. The relay-driver function (FRLY), used to set the mass spectrometer magnet control unit and the amplifier gain switch, is very simple, requiring but two instructions. The argument code determines the relay configuration.

The FOCAL operating programs are written to perform the data acquisition and control with suitable variations for the several instruments, type of sample and its enrichment, and for the precision that is desired. The calculations are performed as usual and include statistical evaluations.

The FADC, the FRLY, and the FCLK routines occupy 55 words in memory. With the elimination of the trigonometric extended-functions, and the overlaying of the space used for the disk monitor-head by the disk swapping routines,[3] there are 1010 locations available for applications programming and in-core storage of variables.

* Presented to and published in the proceedings of the DECUS Fall 1972 Symposium, Royal Inn, Anaheim, California, November 29-December 2, 1972, p. 77.

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DETERMINATION OF SENSITIVITY FACTORS FOR THE SPARK SOURCE MASS SPECTROMETER

E. L. Callis

In broad-range survey-type analyses by spark source mass spectrometry, it is usually assumed that all elements have equal sensitivity. This assumption is probably valid if one is only interested in an accuracy within a factor of 3. For more reliable work, however, one must either use an external standard material of approximately the same composition as the sample being analyzed, or one must determine sensitivity factors for the elements of interest relative to an element which is either present in the sample or is added in a known concentration as an internal standard. At the New Brunswick Laboratory (NBL) a versatile method applicable to various powder samples as well as liquids was desired. Hence, the internal standard method was chosen. The sensitivity factors were measured for an essentially pure graphite matrix with the hope that dilution of a sample with graphite would produce an approximately common matrix. Although yttrium was used as the reference element in the determination of the relative sensitivity factors (RSF), any one of the elements studied can later be used as an internal standard.

EXPERIMENTAL

Instrumentation. The instrument used is an MS-7 (AEI Scientific Apparatus) fitted with electrical detection by the manufacturer. Sparking parameters were: accelerating voltage, 15 kV; pulse repetition rate, 300 p/sec; pulse duration, 200 μsec; spark voltage, 35 kV. The spark gap was manually adjusted by operating the Autospark in the manual mode. The electrodes were not vibrated.

For this work the instrument was operated in the log-ratio scanning mode. In this mode of operation the magnetic field is scanned while the ratio of the electron-multiplier output to the total beam monitor signal is continuously displayed on a ultraviolet beam (UV) recorder. Relative ion intensities are read from the chart paper using a logarithmic scale. The scanning rate was such that the mass range from 240 AMU (atomic mass units) to 9 AMU was covered in about 25 min.

Procedure

Prepare a mixture containing 71 elements at equal concentrations, mostly as the oxides, from Spex Mixes (Spex Industries, Inc., Metuchen, N. J.). Add a sufficient amount of this mixture to high purity graphite powder (Ultra Carbon UCP-1-M) to produce electrodes containing approximately 1000 ppm of each element. Grind this mixture thoroughly and mix in a plastic vial.

RESULTS AND DISCUSSION

The relative sensitivity factors (RSF) are determined by measuring the ratio of the intensity of the major isotope of the unknown element to the reference element, which in this work is monoisotopic yttrium. The general expression relating the various quantities for the unknown and reference elements is

$$(RSF)_{unk} = R_{(j/i)} \cdot \frac{C_{ref}}{C_{unk}} \cdot \frac{(I_i/M)_{ref}}{(I_j/M)_{unk}} \cdot (RSF)_{ref}$$

where i and j refer to the particular isotopes i and j of the reference and unknown elements, respectively;

$R_{(j/i)}$ = ratio of intensities, unknown to reference;

C = weight concentration;

I = isotopic abundance;

M = atomic weight of the respective elements.

It should be noted that no corrections are made for the mass response of the detector or peak width. Hence, the RSF as defined is an overall correction factor.

In Table I are presented the measured sensitivity factors. Each value is the result of 5 determinations corresponding to 5 sample loadings. The reference peak was scanned 6 times for each complete scan of the spectrum.

TABLE I

RELATIVE SENSITIVITY FACTORS DETERMINED IN A GRAPHITE MATRIX

Element	Isotope Used	RSF[a]	RSD, %
U	238	1.8	± 43
Th	232	1.9	± 38
Bi	209	2.1	± 43
Pb	208	4.0	± 33
Tl	205	4.3	± 15
Hg	202	0.5	± 106
Au	197	1.8	± 100
Pt	195	2.1	± 110
Ir	193	1.1	± 61
Re	187	0.4	± 48
W	186	3.3	± 56
Ta	181	1.7	± 56
Hf	180	1.3	± 24

(Table I continued)

TABLE I (Continued)

RELATIVE SENSITIVITY FACTORS DETERMINED IN A GRAPHITE MATRIX

Element	Isotope Used	RSF[a]	RSD, %
Lu	175	1.0	± 14
Yb	174	1.7	± 29
Tm	169	1.1	± 43
Er	166	1.2	± 32
Ho	165	0.93	± 41
Dy	162	1.2	± 41
Tb	159	0.88	± 43
Gd	158	0.86	± 20
Eu	153	0.96	± 13
Sm	152	1.1	± 34
Nd	146	0.83	± 18
Pr	141	0.84	± 20
Ce	140	0.71	± 29
La	139	0.78	± 24
Ba	138	0.97	± 16
Cs	133	3.6	± 30
Te	130	1.3	± 39
I	127	1.3	± 13
Sb	121	1.3	± 32
Sn	120	2.3	± 44
In	115	2.0	± 21
Cd	114	0.78	± 9
Ag	107	2.7	± 23
Pd	106	1.5	± 28
Rh	103	0.7	± 105
Ru	102	0.94	± 31
Mo	98	1.6	± 26
Nb	93	0.98	± 22
Zr	90	1.4	± 33
Sr	88	1.3	± 22
Rb	85	4.2	± 30
Br	81	1.2	± 33
Se	80	1.8	± 37
As	75	1.8	± 27

(Table I continued)

TABLE I (continued)

RELATIVE SENSITIVITY FACTORS DETERMINED IN A GRAPHITE MATRIX

Element	Isotope Used	RSF[a]	RSD, %
Ge	74	1.9	± 52
Ga	69	2.7	± 16
Zn	66	1.6	± 17
Cu	63	1.2	± 41
Ni	58	2.1	± 70
Co	59	2.0	± 11
Fe	56	2.6	± 11
Mn	55	3.5	± 25
Cr	52	2.4	± 17
V	51	1.9	± 27
Ti	48	1.9	± 16
Sc	45	1.9	± 28
Ca	40	2.3	± 36
K	39	7.1	± 28
Cl	37	1.8	± 42
P	31	2.8	± 14
Si	29	3.3	± 25
Al	27	2.7	± 32
Mg	26	3.0	± 9
Na	23	8.1	± 34
F	19	0.5	± 32
B	11	1.6	± 22
Be	9	2.2	± 39
	Averages	1.7[b]	± 29[c]

a. Relative to 1.00 for yttrium

b. Values for Na and K excluded

c. Values for Hg, Au, Pt, Ir, Rh, Ni excluded in the determination of the average precision due to apparent inhomogeneity.

The large relative standard deviations (RSD) of the values for mercury, gold, platinum, iridium, rhodium and nickel indicate that these elements were probably inhomogeneously distributed. The average RSD of 29% for an individual determination is consistant with that reported by other workers[1] using the scanning technique.

In Table II are shown the results of an analysis, using the sensitivity factors in Table I, of U_3O_8 to which impurities had been added.

TABLE II

ANALYSIS OF U_3O_8 SPIKED WITH IMPURITIES

Element	Concentration, ppm	
	Added	Determined
Bi	50	70
Pb	50	70
Hg	50	40
Ba	500	410
Te	50	≤ 100
Sb	50	120
Sn	50	160
In	50	80
Cd	10	≤ 25
Ag	10	14
Mo	500	570
Nb	50	100
Sr	500	520
Rb	500	425
Ge	50	40
Zn	500	450
Cu	50	70
Ni	100	100
Co	50	35
Fe	500	480
Mn	50	40
Cr	100	95
V	500	330
Ti	50	250
Ca	50	75
K	630	570
P	500	425
Si	500	1050
Al	500	850
Mg	50	130
Na	820	940
B	10	14

Gallium at a concentration of 3200 ppm was added as the internal standard. The agreement between the measured and added values for impurities at the 100 ppm and above level appears to be good, the average deviation being less than 14% if the values for silicon and aluminum are excluded. The large discrepancies in the cases of titanium, aluminum and silicon are not understood. The relatively poorer agreement for the 50- and 10-ppm levels may be due to the peak intensities being measured at gain settings too low for reliable results.

In Table III are shown the results of an analysis of a synthetic mineral sample. The matrix of 70% silica, 20% iron oxide, and 10% calcium carbonate was spiked with oxide impurities, and 500 ppm gallium was added as the internal standard.

TABLE III

ANALYSIS OF A SYNTHETIC MINERAL SAMPLE

Element	Quantity Added, ppm	Determined, ppm	Ratio, Determined / Added
Si[a]	(32.7%)	(13%)	--
Fe	(14.0%)	(13%)	--
Ca	(4.0%)	(4.1%)	--
Hg	500	590	1.18
Cd	500	425	0.85
Mo	500	410	0.82
Se	1000	870	0.87
As	100	150	1.50
Zn	500	510	1.02
Cu	100	135	1.35
Co	500	330	0.66
Mn	100	100	1.00
V	100	95	0.95
Al	500	650	1.30
Na	500	270	0.54
		Average Ratio	1.00
		RSD, %	29

a. Matrix elements Si, Fe and Ca included for information only.

It is interesting to note the low value for the matrix element Si. Low values for silicon have been observed at NBL in other analyses of this matrix using the internal standard technique. The low results are believed to be due to a significant broadening of the ion energy distributions at matrix level concentrations causing a smaller fraction of the ions of a given element to be transmitted by the monitor into the magnetic analyzer.

For the added impurity elements, the ratio of the determined to the added value has been calculated. The average value of 1.00 for this quantity is reassuring and the RSD of 29% is consistant with the precisions observed in the determinations of the sensitivity factors.

Based on the limited analyses presented in this report it would appear that relative sensitivity factors determined for a graphite matrix are, in most cases, valid also for 1:1 sample-graphite electrodes. The relationships probably break down, however, at concentrations approaching matrix levels.

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1. Bingham, R. A. and Elliott, R. M., Anal. Chem., 43, 44 (1971).

SPARK SOURCE MASS SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN URANIUM HEXAFLUORIDE — A PROGRESS REPORT

E. L. Callis

Development of a spark source mass spectrographic technique for the determination of volatile impurities in uranium hexafluoride (UF_6) is currently underway at the New Brunswick Laboratory (NBL). The technique involves the introduction of gaseous uranium hexafluoride into a spark gap where it is ionized. The primary advantage of this method of analysis is the fact that no chemical separations or conversions are required.

In a previous report[1] the preliminary work on this project was described. Recently, an improved inlet system has been constructed which allows a small quantity of uranium hexafluoride to be heated to a maximum of 300°C and admitted into the ion source. Since the inlet system is "floated" at the accelerating potential of 15 kV, an isolated power unit was built to supply power to the heating tapes which are used to heat the system. The only serious problem encountered so far is the radiation of spark noise by the system. It is felt that this can be overcome by proper shielding.

Another improvement has been the fabrication of various source parts of nickel and Monel to replace the conventional tantalum parts. This permits the determination of tantalum as an impurity.

Work on a Uranium Hexafluoride Impurity Standard. To obtain quantitative results using this direct ionization technique, uranium hexafluoride containing known amounts of impurities is needed. An attempt was made to produce such a material by adding impurities in the elemental form to the uranium hexafluoride and heating in a fluorination tube to 300°C. Several of the elements were detected in the mass spectrum and appeared to have converted quantitatively while others were detected at much lower concentrations than were added or were not detected at all.

Future work will be directed toward devising a method for the production of a reliable reference material and, in general, the development of an overall analysis technique which will permit routine analysis.

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

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EVALUATION OF THE FABRY-PEROT INTERFERENCE SPECTROMETER FOR URANIUM ISOTOPIC ANALYSIS — A STATUS REPORT

H. G. Yuster

In a previous report[1] a commercial Fabry-Perot interference spectrometer manufactured by Jobin-Yvon Company in France was evaluated for the determination of uranium isotopic abundance. The results obtained at that time can be briefly summarized as follows. The speed of analysis is relatively slow because a single hollow cathode excitation source is used which requires prior conditioning before the measurements. In addition the technique of pressure scanning is an inherently slow process when adiabatic conditions must be met. This latter factor, which leads to long time intervals between peak measurements and necessitates taking the average of many peak ratios, is responsible, at least in part, for the poor precision obtained despite the fact that the hollow cathode source is relatively stable.

Three modifications to the basic instrumentation are in progress. First, a 6-unit hollow cathode cluster of the turret type as shown in Figure 1 and 2 has been constructed to replace the single unit presently used. With this system, one hollow cathode can be in the measurement mode while the remaining five are being conditioned at reduced amperage. The unit is powered by a regulated 550 VDC and 500 mA supply with controls for the amperage and individual ammeter monitoring of each cathode. The maximum amperage on one hollow cathode is about 80 mA. Ball-bearing detents allow the cluster to be rotated so that each hollow cathode can be placed in the optical path. Second, a piezo-electric unit with a special ramp generator has been ordered for the rapid scanning of the etalon plate. Third, a digital voltmeter with printer is being obtained. These latter two items will materially speed up the scanning and measurements and hopefully will improve the precision of the data.

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1. Yuster, H. G., NBL-265 (October 1972), p. 74.

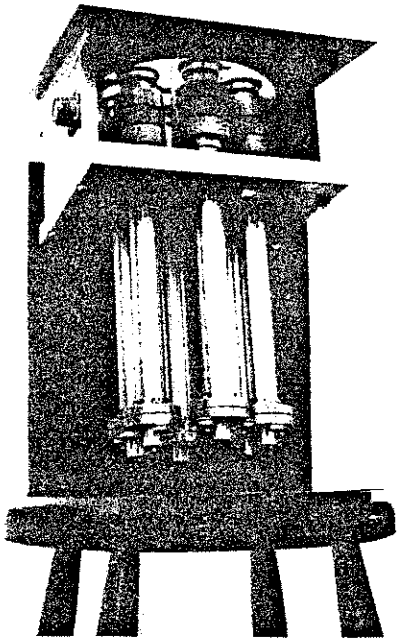


FIGURE 1. PHOTOGRAPH OF HOLLOW CATHODE CLUSTER — SIDE VIEW.

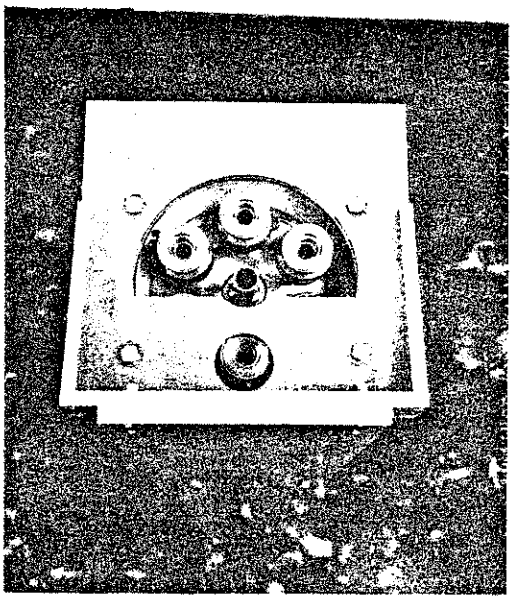


FIGURE 2. TOP VIEW OF CLUSTER SHOWING ONE CATHODE IN OPTICAL PATH (ROUND HOLE).

A CENTRAL ANNUNCIATOR PANEL FOR THE NEW BRUNSWICK LABORATORY — A PROGRESS REPORT

R. J. Hemmer

Under the previous alarm system at the New Brunswick Laboratory (NBL), abnormal instrumental readings or malfunctions would set off the following audio or visual alarms: Fire, Smoke, Stack Monitor, Waste Tank, Differential Pressure, Gamma Monitor, Air Monitor, Stack Flow, Air Pressure and Freeze. Some of these alarms were laboratory-wide, others were only local. The various alarms of this system, added piece-meal as the need arose, were confusing and, in some cases, ineffective because of problems associated with the fact that the laboratory consists of two separate buildings.

The present report describes the planned consolidation of all these alarms into one master panel located in the main laboratory with a repeater panel located in the second building. The various alarms are given one of three different priorities indicated by the color of the lighted display on the panels and by a distinct audio signal. The completed system will be generally more efficient and less confusing than the original one.

General Design and Operation

The master panel is located in the lobby of the main building directly behind the telephone switchboard and public address system. This location is optimum for alerting the operator or guard on duty who will have quick access to the internal or external communication lines. With the NBL-designed panel, only the floor plan of the laboratory and the motor status display are shown under a no-alarm condition. The repeater panel is located in the entrance way of the second building behind the main building.

The master panel is shown in Figure 1. When an alarm is tripped, the type of alarm, Smoke, Fire, etc., is indicated by lighted displays on the left side of the panel, and the location of the condition is lighted on the floor plan, Figure 2. An audio signal sounds. Both visual and audio alarms continue until manually shut off.

One of three priorities are assigned to an alarm to indicate the seriousness of the emergency. Level 1 denotes a criticality incident shown by a Gamma Monitor pair. The audio alarm is a wavering siren and the panel lighting color for this level is green. Under level 1, all personnel evacuate immediately.

A laboratory-wide alert is assigned level 2. The audio alarm is a claxon horn and the panel lighting is red. Under level 2, all personnel make preparation to evacuate and wait instruction. These instructions to personnel are given over the public address

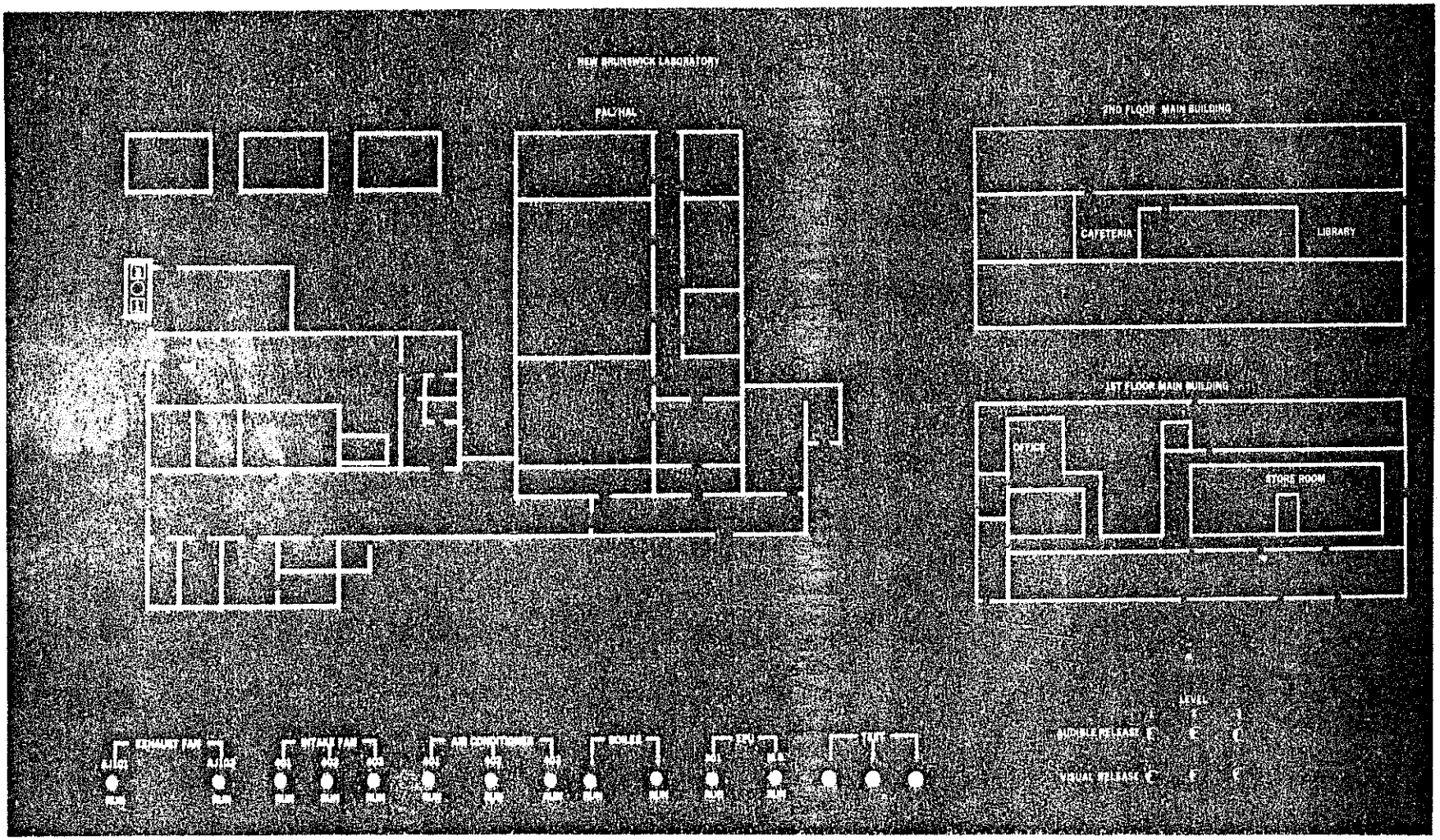


FIGURE 1. PANEL UNDER NO ALARM CONDITION.

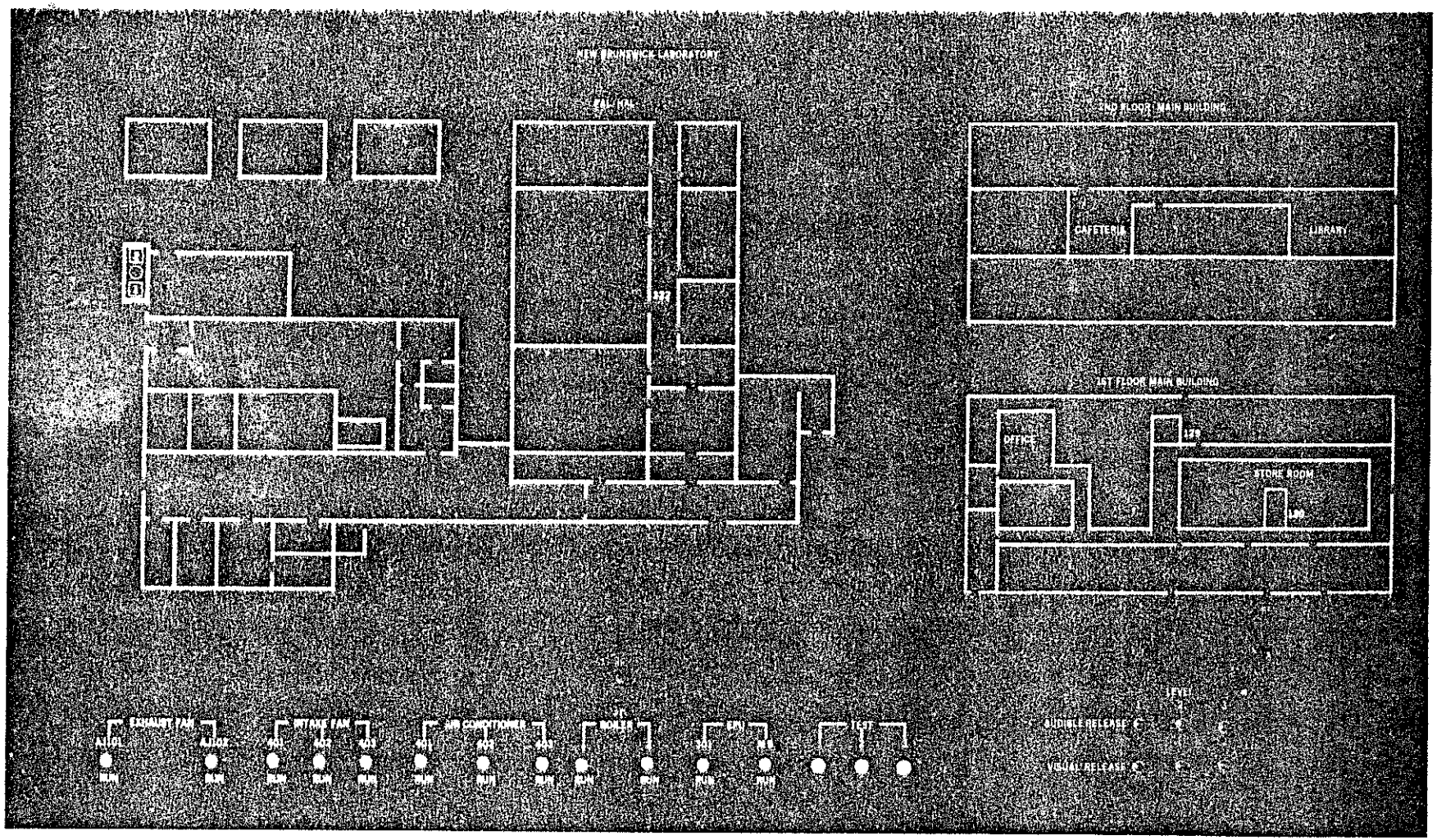


FIGURE 2. PANEL WITH ROOMS 120, 129 AND 322 GIVING A GAMMA MONITOR ALARM.

system. The alarms assigned priority level 2 are the Stack Monitor (High-level), Fire, Air Monitor, and single Gamma Monitor.

Level 3 indicates a non-emergency condition requiring action by certain laboratory personnel. Information and instructions, as required, are again given over the public address system. The alarm is a continuously ringing bell and the lighting color is orange. These alarms include the Stack Flow, Differential Pressure, Waste Tank, Smoke, Stack Monitor (low-level), Gamma Monitor, Freeze, Air, and Air Monitor.

The master panel contains all the circuitry necessary for the alarm operation, for the testing of the 3 levels individually, for silencing the audible alarms, and for resetting the visual indicators. The repeater panel merely repeats the lighting on the master panel.

Figure 3 indicates how a FIRE alarm originating in Room 308 activates the master panel: Switch S1 closes and energizes relay K1 which causes the visual and audio alarms to be activated. Relay K_2 is much faster than relay K1, thus allowing it to operate. Relay K_2 operates the horn; Switch S2 deactivates the horn for testing, while lamp I1 indicates proper operation of relay K3. The red room number 308 is used by three different level-2 alarms; therefore, diodes are used to isolate the three systems.

Status. The panels have been in operation for the past three months with the Fire and Gamma Monitor (Criticality) alarms connected. Operation has been satisfactory even during a temporary power failure. The other functions will be added as quickly as time permits.

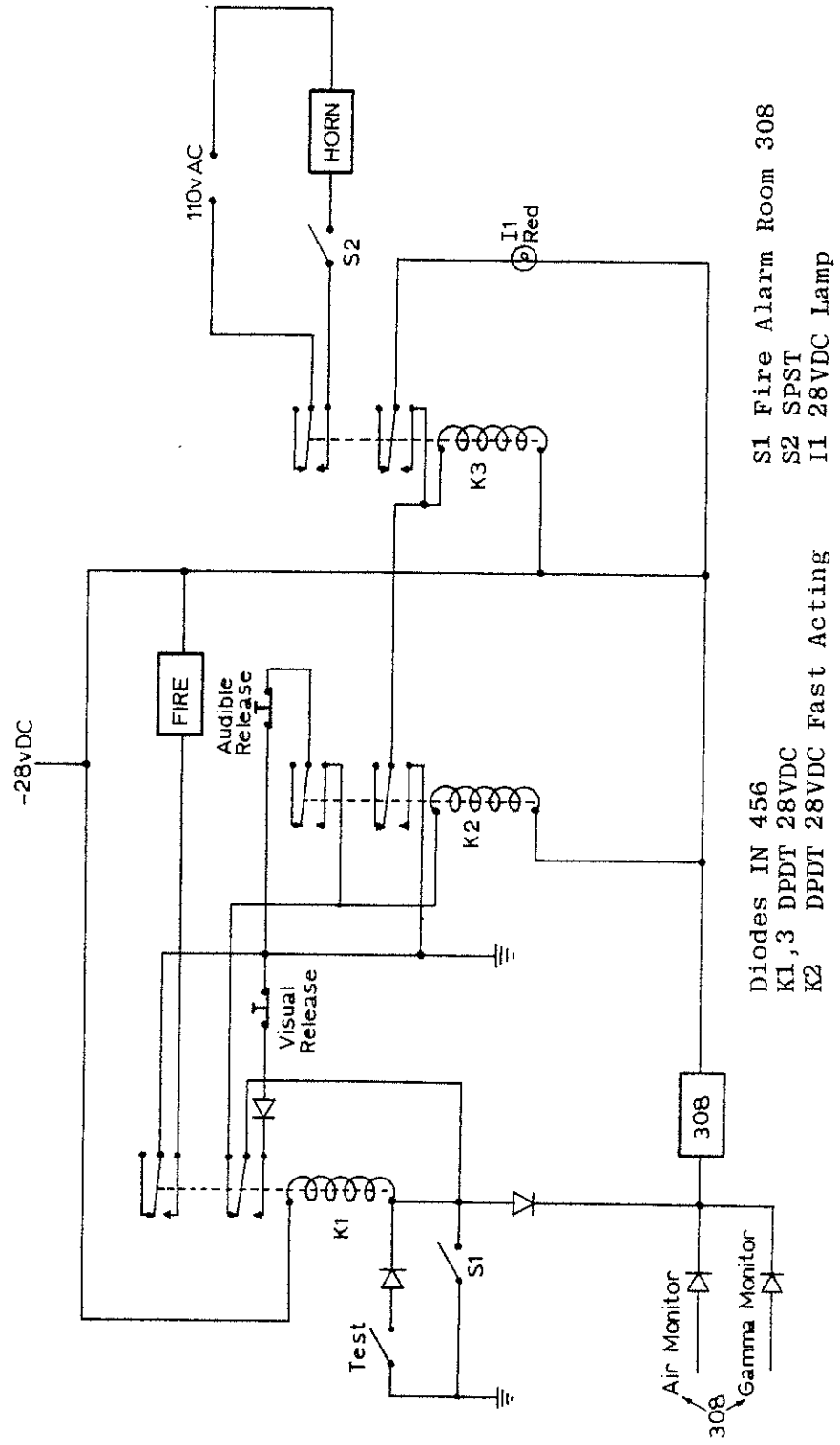


FIGURE 3. TYPICAL ALARM TRIP CIRCUIT.

AN AUTOMATED MINI ION-EXCHANGE AND COULOMETRY SYSTEM — A PROGRESS REPORT

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

Although controlled-potential coulometry is adversely affected by few elements, many plutonium samples are not readily analyzed by this method because of their high salt and impurity content. A separation of plutonium from impurities is considered necessary for reliable results.[1,2]

A large increase in the number of plutonium samples analyzed in the nuclear field is anticipated in the next few years. To meet these demands with a minimum increase in operating costs and no loss in quality, the New Brunswick Laboratory (NBL) is developing two related automated systems.

The first system (Autosep) automates the mini ion-exchange separation of plutonium from interferences. The second system (Autocoulometry) automates the controlled-potential coulometric determination of plutonium in the separated samples. These two systems are based on procedures previously described.[1]

The present report, preliminary in nature, describes the project and gives the status of the fabrication.

Autosep System

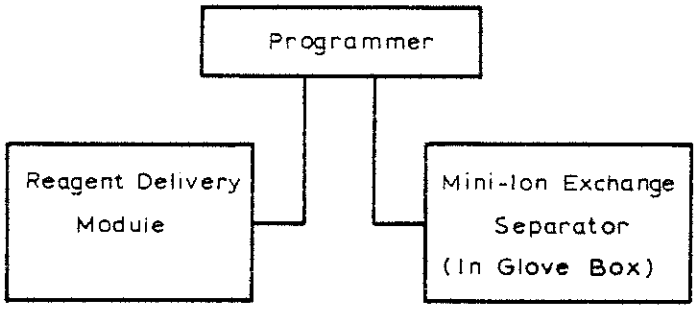
The Autosep system is designed as a batch-type operation in which 10 sample aliquots are simultaneously passed through ion-exchange columns. Weighed aliquots of dissolved sample, each containing 5-10 mg of plutonium, are added to each of 10 reservoirs in the mini-ion exchange separator. The volume of liquid in each reservoir is brought to 10 ml by addition of a reagent and all subsequent steps in the separation are done automatically. The system incorporates a means of programming adjustment to the plutonium(IV) oxidation state, reagent delivery, column loading and washing, and stripping of the mini-ion exchange columns. The reagents are delivered by gravity from a module whose only moving parts are solenoid valves. The eluted plutonium solutions are collected in glass coulometer cells held in stainless steel trays.

The Autosep system consists of 3 modules, an Agastat programmer, a reagent delivery module, and a mini ion-exchange separator, Figure 1. Only the mini-ion exchange separator must be inside a glove box.

Autocoulometry System

The Autocoulometry system has a sample-handling apparatus capable of 100 samples per loading. Samples are loaded onto the

AUTOSEP SYSTEM



AUTOCOULOMETRY SYSTEM

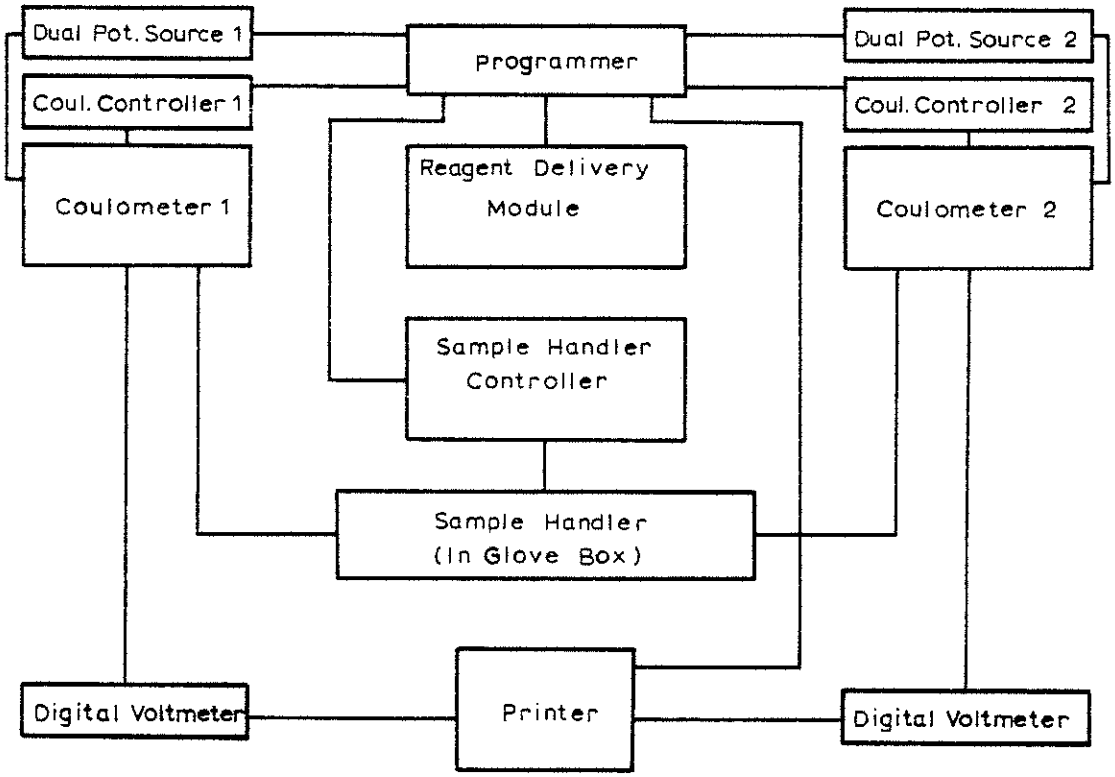


FIGURE 1.
BLOCK DIAGRAM OF AUTOSEP AND AUTOCOULOMETRY SYSTEMS

unit in stainless steel trays, each tray containing 5 glass coulometer cells with each cell holding a plutonium sample. The unit has dual cell heads which operate simultaneously, and a controlled potential coulometer for each head. The sample handler, by means of conveyor systems, moves the trays such that cells are sequentially placed under the cell heads, the cell heads are lowered into place, and the programmer is advanced to the next operation. Ten trays are run by each head per loading. The system has provisions for automatically determining separate blanks for each sample, controlling the coulometric determination, combining analyzed samples for recovery of plutonium, cleaning all coulometer cells for re-use, and printing data.

The Autocoulometry system consists of 13 modules including an Agastat programmer, a reagent delivery module, a sample handler, a sample-handler controller, 2 dual-potential source units, 2 coulometer controllers, 2 controlled-potential coulometers, 2 digital voltmeters, and a printer, Figure 1. Only the sample handler must be inside a glove box.

DISCUSSION

Maintenance was considered in designing the systems, and standard commercially available parts were used where possible. An effort was made to select materials for the units in the glove boxes which would be most resistant to an acid environment. This factor led to the use of sealed switches and plastic or stainless steel parts where feasible.

The Autosep and Autocoulometry systems, although in a preliminary stage, show much promise in meeting our goal of increased high-quality output without the need for more glove box space or additional personnel. It is estimated that a 3 to 5 fold increase in productivity, with the same size staff, will result with less glove-box space requirement than that needed for the existing operations. The Autocoulometry system has the capability of operating 24 hours a day. The increased sample capacity using the two systems should allow several determinations on each sample to be made and allow a calculation of the precision of the results.

Status

At present, the modules composing the two systems are in various stages of construction. The parts for the reagent-delivery modules for both systems are on hand and await assembly. The sample-handler controller for Autocoulometry is designed but is not yet assembled since the sample handler itself is still under construction. Delivery of the dual-potential source units and the coulometer controllers for Autocoulometry, designed and built at Lawrence Livermore Laboratory, is expected in the near future. The mini-ion exchange separator for Autosep is almost completed. The remaining modules are on hand and operational.

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CALCULATION OF HYDROGEN GENERATION FROM PLUTONIUM-INDUCED RADIOLYSIS OF NITRIC, SULFURIC AND PERCHLORIC ACIDS

J. R. Weiss and C. E. Pietri

The products of radiolysis in an aqueous system vary with the type of radiation and the particular solutes present in the solution. Plutonium in aqueous solution causes radiolytic generation of several gases including hydrogen which in stored solutions presents an explosion hazard. To evaluate the magnitude of such a hazard, it is necessary to predict the rate of hydrogen generation. In a previous report,[1] these calculations were made for a dilute sulfuric acid solution of plutonium held in a storage assembly with several different venting configurations. In the present study, an existing equation[2] was modified to permit calculation of the hydrogen generation in various concentrations of nitric, sulfuric and perchloric acid and various concentrations and isotopic compositions of plutonium.

The modified equation to calculate the hydrogen generation is as follows:

$$H_2\,(\text{moles/day}) = (1.675 \times 10^{-5})\ (Pu)(G)(C)$$

where Pu = quantity of plutonium in the solution, g;

G = hydrogen evolved per 100 electron volts of energy absorbed by the system, molecules;

and

$$C = 0.01\ (302.0\ [^{238}Pu(\%)] + 1.000\ [^{239}Pu(\%)] + 3.696\ [^{240}Pu(\%)] + 0.0417\ [^{241}Pu(\%)] + 0.0604\ [^{242}Pu(\%)])$$

with the isotopic compositions expressed as weight per cent.

The data indicate that plutonium in nitric or perchloric acid generates considerably less hydrogen than in sulfuric acid. For example, 50 g of plutonium consisting of 0.7% plutonium-238, 41% plutonium-239, 43% plutonium-240, 10.4% plutonium-241 and 4.9% plutonium-242 produces 16 ml/day (STP) of hydrogen in 1M nitric acid, 29 ml/day in 1M perchloric acid, and 124 ml/day in 0.1M sulfuric acid. A calculation for 1M sulfuric acid could not be carried out because of the lack of pertinent data, but it is estimated that the hydrogen generation at this concentration would be only slightly lower than 124 ml/day.

This same 50 g of plutonium in 10M nitric acid produces only 1.4 ml/day of hydrogen. Thus it is clear that there is a considerable advantage in storing plutonium in solutions of high nitric acid concentration in order to avoid high hydrogen generation rates and thereby minimize the explosion hazard.

A detailed account of this study has been accepted for publication in Radiation Effects.

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A GENERAL ANALYTICAL EVALUATION (GAE) PROGRAM FOR URANIUM HEXAFLUORIDE

C. D. Bingham

A program has been planned and placed into operation to demonstrate whether a consistent level of performance exists in the chemical assay and measurement of isotopic abundance of uranium in uranium hexafluoride (UF_6). Some of those organizations presently involved or likely to become involved in toll-enrichment transactions as well as fuel reprocessing or conversion facilities have been invited to participate.

Phase I of the program involves measuring the uranium content and isotopic abundance each month in each of three samples ranging from near-normal to approximately 2% enrichment in uranium-235. Phase I sample distribution began in June 1973 and will continue for 14 months. Nine domestic and 11 foreign laboratories are currently participating in Phase I.

Phase I samples for uranium assay are being distributed in fluorothene ("P-10") tubes, Figure 1. Samples for uranium isotopic abundance measurements are being distributed in heat-sealed polyethylene ("pig tail") tubes.

Phase II will consist of similar measurements made upon material taken as sub-samples from 15 containers to assess the contribution of sampling to the overall variance of measurement. A Phase III will involve measurement of impurity element content in samples of uranium hexafluoride. A firm time schedule for Phases II and III has not been established, pending experiences observed in Phase I.

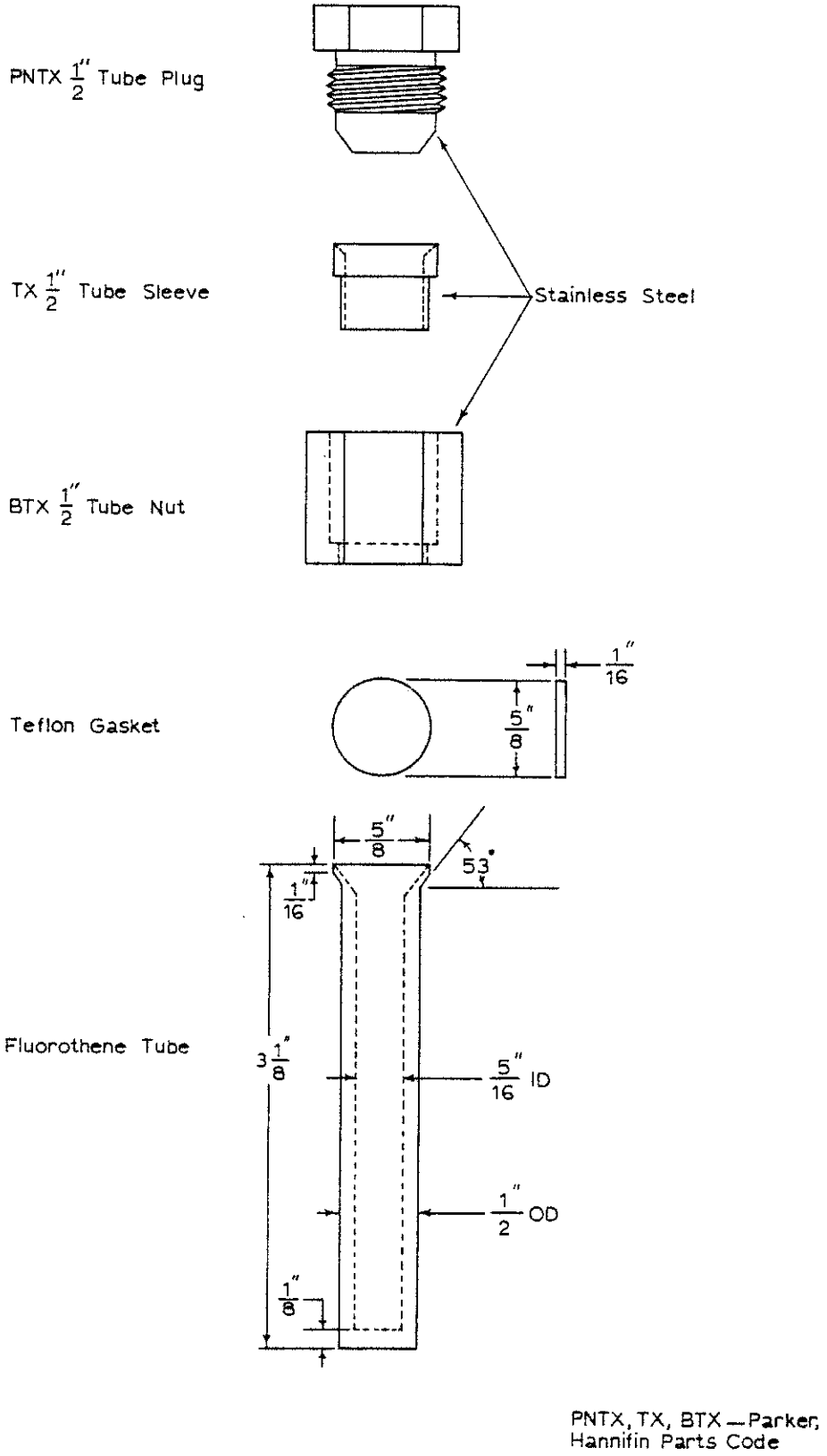

FIGURE 1. FLUOROTHENE (P-10) TUBE.

A TENTATIVE METHOD FOR THE SPECTROCHEMICAL DETERMINATION OF MERCURY AND ARSENIC IN A SYNTHETIC ENVIRONMENTAL TEST MATERIAL

H. G. Yuster

An environmental test material consisting of 70% silica, 20% ferric oxide, and 10% calcium carbonate containing various impurities at known levels was prepared at the New Brunswick Laboratory (NBL). This material was one of two test samples to be used in an interlaboratory evaluation program designed to test the reliability of activation procedures utilizing californium-252. To confirm the levels of the various impurities obtained by addition to the base material, a variety of methods was used to analyze the final mixture.

For the spectrochemical determination of mercury and arsenic, no standards were available. Attempts to prepare standards from the matrix material indicated that the mixing after the addition of mercury, arsenic and the proposed internal standard tellurium would be very tedious. The spiked powder balled up and tended to stick to the mortar tenaciously. Therefore, the standards were prepared in U_3O_8 which can be very smoothly homogenized after spiking. The final procedure involved the addition of the test material to U_3O_8 and comparing the data obtained with this mixture to that obtained with U_3O_8 standards, containing mercury, arsenic and tellurium, mixed with the blank matrix material. The boiler-cap technique was used for the spectral excitation.

EXPERIMENTAL

Reagents and Apparatus

All reagents are reagent-grade.

U_3O_8, high-purity

Vials, plexiglass, 1/2 in. diameter by 1 in. long, with 3/8 in. plastic ball.

Mixer Mill, Wiggle-Bug, Spex Industries.

Spectrograph, Jarrell-Ash, 3.4 m Ebert, with a reciprocal linear dispersion of 5 Å/mm.

Densitometer. Jarrel-Ash Microphotometer.

Standards Preparation. Prepare a solution of the internal standard tellurium by dissolving the metal in 1:1 HCl to obtain a concentration of 10 mg/ml. Add 1.00 ml of this solution to 10 g of U_3O_8

to give a 1000 ppm concentration. Dry the mixture at 110°C for 1 hr. Grind and scrape down in an agate mortar in the usual way to obtain a well-homogenized mixture. To this mixture add appropriate aliquots of solutions of mercuric chloride and arsenious oxide, basing the calculation on the use of 20 mg of base material to 980 g of the U_3O_8 to obtain the following concentrations in the final mixture:

Concentration, ppm		
Hg	As	Te
900	200	1000
450	100	1000
225	50	1000
113	25	1000
0	0	1000

Dry and homogenize the U_3O_8 mixture in the usual way.

Sample Preparation. Add 20 mg of sample to 980 g of U_3O_8 in a plastic vial containing a plastic ball and mix in a Wiggle-Bug for 60 sec.

Analytical Conditions

Source - Set for 15 A (shorted) at 300 VDC
Gap - 4 mm
Charge - 200 mg, punched with venting tool
Electrodes - Upper ASTM C-1
- Lower ASTM S-2
- Pedestal ASTM S-1
- Boiler Cap UCC
Exposure - 30 sec (no prearc)
Plates - Eastman Kodak Spectrum Analyzer No. 1
Wavelength - 2200-3400 Å
Processing - According to ASTM E115 recommendations
Analytical Lines - Hg - 2536.52 Å
- As - 2780.22 Å
- Te - 2385.76 Å (Internal Standard for Hg)

RESULTS AND DISCUSSION

The results obtained with 3 replicate analyses on the test material as compared with the chemical analytical results and the quantities added are shown in Table I. Only the mercury line was densitometered.

TABLE I

RESULTS OBTAINED ON THE PREPARED SOLID TEST MATERIAL

	Concentration, ppm		
Element	Found (Average)	(Chemical)[1]	Added
Hg	670	560	573
As	50[a]	35	37

a. Visual estimation.

The range of results on the mercury determination was about 5%. These values are satisfactory considering the fact that the spectrochemical results were obtained chiefly to confirm the quantities of mercury and arsenic added. For routine use, additional work would probably be necessary to make the procedure more precise and accurate.

REFERENCE

1. Trahey, N. M., Scarborough, J. M. and Bodnar, L. Z., NBL-267 (September 1973), p. 56.

BACKGROUND CORRECTION IN EMISSION SPECTROSCOPY

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The correction of line intensity for background effects when photographic plates are used is often difficult. Slavin[1] states that an exact correction is impossible. However, it is generally agreed that some form of background correction is desirable even when samples and standards are of similar composition.

Comprehensive discussions of background correction have been given by Ahrens,[2] and by the American Society for Testing and Materials (ASTM).[3] One method described involves taking the average of the corrections on both sides of the line. This method requires that readings be taken at equidistant points from the analytical line. Also, the assumption must be made that the monochromatic and continuous radiation, if both are present, have equal photographic response.

In the following mathematical treatment of background correction, densitometric measurements on both sides of the analytical line are considered. The basic equation in densitometry relates transmission T to line density D by the equation:

$$D = \log_{10} 100 - \log_{10} T \qquad (1)$$

The density of an analytical line corrected for the average background density of both the right and left side can thus be expressed as:

$$D_C = D_M - \left(\frac{D_R + D_L}{2}\right) \qquad (2)$$

where subscript C = corrected,

and M = measured.

Combining equations (1) and (2) one obtains the relationship in terms of T, the measurement obtained by a densitometer:

$$T_C = \frac{100\ T_M}{(T_R\ T_L)^{1/2}} \qquad (3)$$

With the use of equation (3), per cent transmission measurements can be used to obtain easily a corrected T_C value for the determination of log relative intensity values in the plot of analytical curves. Previously, background and line per cent transmission values were converted to densities so that the correction could be made, and then the corrected density was converted back to T_C.

To obtain more valid corrections it is desirable to use a step sector and choose transmission readings between 30 and 70. All readings should be made in the same step.

REFERENCES

1. Slavin, M., "Emission Spectrochemical Analysis," Vol. 36, Wiley-Interscience, New York, N.Y., (1971), pp. 196-197.

2. Ahrens, L. H. and Taylor, S. R., "Spectrochemical Analysis," 2nd Ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., (1961), pp. 164-169.

3. "Methods of Emission Spectrochemical Analysis," 5th Ed.,Am. Soc. Testing Mat., Philadelphia, Pa., (1968), pp. 159-163.