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NEW BRUNSWICK LABORATORY

Carleton D. Bingham, Director

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ABSTRACTS

The Effect of Impurities on the NBL Titrimetric Method of Determining Uranium

The last of a series of reports on the effect of impurities on the titrimetric determination is presented. Twenty-three additional elements were investigated; none produced significant interference effects.

The Effect of Technetium on the NBL Method of Determining Uranium - A Joint Effort with Oak Ridge National Laboratory

The assay of HTGR recycle fuel may involve the analysis of uranium which contains technetium-99. Methods of removing Tc from uranium samples are discussed.

The Effect of High Alpha Activity on the New Brunswick Laboratory Titrimetric Method of Determining Uranium - A Joint Effort with Oak Ridge National Laboratory

HTGR recycle fuel may contain significant quantities of U-232. The effect of high density alpha activity on the NBL titrimetric method of determining uranium was investigated.

The Determination of Uranium in Fissium-Uranium Alloy and in Fissium Dross

Dissolution and analysis techniques for fissium-uranium alloy and fissium dross are described.

Determination of Uranium Following Reduction with Iron(II) in Phosphoric Acid Utilizing Amperometric End-Point Detection

A procedure for the determination of 1 to 5-mg quantities of uranium which combines potentiometry and amperometry is described. Results are free of bias with coefficients of variation of less than 0.1%.

Determination of Uranium in Hard-to-Dissolve Residues by X-ray Fluorescence

A rapid X-ray fluorescence technique for the determination of uranium in calcined ash samples is discussed.

The Determination of Uranium in Scrap Materials by Isotope Dilution Mass Spectrometry

A procedure is described for the determination of uranium in calcined ash samples by isotope dilution mass spectrometry.

Computer Simulation of HTGR Fuel Microspheres Using A Monte-Carlo Statistical Approach

The concept and computational aspects of a Monte-Carlo statistical approach in relating structure of HTGR fuel microspheres to the uranium content of fuel samples have been verified. Results of the preliminary validation tests and the benefits to be derived from the program are summarized.

A Volume-Dependent Count Correction Factor for the Delayed Neutron Analysis of Uranium-235

The derivation of a volume-dependent count correction factor for the delayed neutron analysis of uranium-235 is described.

An Evaluation of the New Brunswick Laboratory 12" 60° Mass Spectrometer Using a National Bureau of Standards Style System Calibration

A study to demonstrate the performance capabilities of NBL mass spectrometer instrumentation using a National Bureau of Standards calibration procedure is discussed.

The Evaluation of the Los Alamos Scientific Laboratory Bomb Sample Dissolution Technique and Automated Extraction Spectrophotometer for Uranium Assay

A system for the automated analysis of uranium samples, developed by the Los Alamos Scientific Laboratory (LASL), has been evaluated for ERDA and LASL at the New Brunswick Laboratory. The system consisted of a bomb dissolution technique employing a teflon-lined Parr bomb, filtration of sample solution, gamma counting of the residue to determine its uranium content, and assay of the filtrate for uranium by an automated extraction spectrophotometer. Tests and test results are described.

A Laboratory Quality Assurance Program for Uranium Assay

Abstract of NBL-276 (June 1975).

Preparation of Standard "Unknown" Samples for Measurement Control

A procedure is provided for the preparation of quality assurance standards for control of uranium measurements at NBL.

Interlaboratory Evaluation on Measurements of Uranium Hexafluoride

Abstract of NBL-274 (May 1975).

Status of Phase II of the Interlaboratory Comparison Program on the Analysis of HTGR Fuel

A summary of the status of the subject program is provided.

Colorimetric Determination of Iron in Uranium Oxide with Ferrozine

A simple but effective procedure for the determination of iron in the presence of uranium with ferrozine is described.

Time Resolved Studies for the Evolution of Elements by Carrier Distillation from Uranium Oxide

Abstract of paper prepared for publication.

The Determination of Magnesium in Beryllium by Atomic Absorption Spectrometry

A procedure is described for the determination of magnesium in beryllium by atomic absorption spectrophotometry which eliminates the hazards associated with the aspiration of beryllium into the burner of the instrument.

An Investigation of the Long-Term Reliability and Reproducibility of a Controlled-Potential Coulometric Method Proposed for the Determination of Plutonium

Work is described in which experiments with iron were performed to assess the long-term reliability and reproducibility of coulometric measurements. Procedures are included for instrument calibration and electrode conditioning.

Preliminary Evaluation of an Automated Coulometry System (Autocoulometry) for Plutonium

The testing of the mechanical and electrical performance of the NBL autocoulometry system for Pu assay is described.

The Response of Gold Electrodes for Use in Controlled-Potential Coulometry

The operating characteristics of three hand-crafted gold working electrodes were evaluated for use in controlled-potential coulometry.

The Effect of Ion-Exchange Separation Procedures on Controlled-Potential Coulometric Analysis

A systematic study of the effect of ion-exchange separation procedures on the controlled-potential coulometric determination of plutonium is described.

THE EFFECT OF IMPURITIES ON THE NBL TITRIMETRIC METHOD OF DETERMINING URANIUM

L. Z. Bodnar

A series of previous reports¹⁻⁵ discussed the effects of various elements and compounds on the accuracy of determining uranium by the NBL titrimetric method. This report is the last in this series. In it is contained a summary of the studies involving zinc, cadmium, magnesium, calcium, barium, lutetium, europium, rhenium, cesium, scandium, gallium, germanium, lanthanum, yttrium, strontium, praseodymium, gadolinium, erbium, ytterbium, tungsten, tellurium, thallium, and selenium.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus used in the NBL method are described in a previous report.⁶

Uranium Standards. Nitric-sulfuric acid solution of NBL dingot uranium metal, ~ 10 mg U/g.

Impurity Stock Solutions. Aqueous/acid solutions of Zn, Cd, Mg, Ca, Ba, Lu, Eu, Re, Cs, Sc, Ga, Ge, La, Y, Sr, Pr, Gd, Er, Yb, W, Te, Tl, Se; concentration, 1-10 mg/ml.

Procedure

Transfer weighed aliquants of uranium standard solution, each containing approximately 100 mg of uranium, to 400 ml beakers and evaporate to dryness on a steambath. After adding appropriate amounts of impurities, reconstitute and adjust these standards to a 15 ml volume with appropriate solvents. Proceed with the NBL titrimetric method for determining uranium in the usual manner.

RESULTS AND DISCUSSION

The data obtained from the determinations of known amounts of uranium, containing various added amounts of impurities, are shown in Table I. Although 5 to 50-mg quantities of impurities were tested, only the highest impurity levels are reported in Table I except for Ba. Higher concentrations of impurities are improbable and were therefore not investigated. None of the elements reported here, except for Ba, interfere with the NBL titrimetric procedure when present up to the maximum levels reported in Table I in a standard containing 100 mg of uranium. Barium, when present in ratios greater than 15 mg to 100 mg of uranium, will precipitate as a sulfate (present in the titration medium) and cause

TABLE I

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

<u>Impurity Element</u>	<u>Quantity of Impurity,mg</u>	<u>Quantity of U Added, mg</u>	<u>Quantity of U Found, mg</u>	<u>Relative Error, %^a</u>
Ba	5	102.60	102.55	-0.05
	10	102.29	102.23	-0.06
	15	101.60	101.52	-0.08
	25	103.00	102.65	-0.34
	50	102.91	102.65	-0.26
Cd	50	104.18	104.15	-0.02
Ca	50	102.58	102.55	-0.03
Cs	50	104.79	104.78	-0.01
Er	50	103.59	103.54	-0.04
Eu	25	102.71	102.70	-0.01
Gd	50	104.84	104.87	+0.03
Ga	50	104.70	104.69	-0.01
Ge	50	103.08	103.08	0
La	25	103.88	103.87	-0.01
Lu	25	106.66	106.66	0
Mg	50	102.99	103.00	+0.01
Pr	25	103.13	103.12	-0.01
Re	20	102.76	102.86	+0.10
Sc	25	104.28	104.24	-0.04
Se	20	113.09	113.09	0
Sr	20	103.59	103.64	+0.05
Ta	50	103.12	103.11	-0.01
Te	50	102.92	102.95	+0.03
Tl	50	104.30	104.33	+0.03
W	50	105.43	105.43	0
Yb	50	102.89	102.93	+0.04
Y	50	103.93	103.93	0
Zn	50	101.62	101.62	0

a. Relative Error, % = $\frac{\text{Amount of U Found}-\text{Amount in Std.}}{\text{Amount in Std.}} \times 100$

serious low results as indicated in Table I. Small quantities of uranium are carried down by the precipitate. However, it is uncommon for samples to contain more than 15 per cent barium.

Only a representative number of rare earth elements which were readily available were investigated since the chemical properties of these elements are nearly identical and interference effects are similar.

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. 26.
3. Scarborough, J. M., NBL-265 (October 1972), p. 26.
4. Scarborough, J. M. and Bodnar, L. Z., NBL-267 (September 1973), p. 6.
5. Bodnar, L. Z., Lerner, M. W. and Scarborough, J. M., NBL-272 (October 1974) p. 5.
6. NBL-272, Appendix (A) (October 1974), p. 113.

THE EFFECT OF TECHNETIUM ON THE NBL METHOD OF
DETERMINING URANIUM - A JOINT EFFORT WITH
OAK RIDGE NATIONAL LABORATORY

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The assay of HTGR recycle fuel may involve the analysis of uranium which contains technetium-99 as well as uranium-232.¹ The effect of these substances on the accuracy of uranium measurements must therefore be assessed. Technetium is covered in this report; alpha activity from ^{232}U is treated in a separate report.¹

Since many of the chemical properties of technetium lie somewhere between those of manganese (a serious interferent in the NBL titrimetric method) and rhenium (a non-interferent), its behavior is difficult to predict. Experiments were performed to determine whether technetium interferes with the NBL method and if so, to develop an effective means for eliminating the observed interference.

Reagents and Apparatus

The reagents and apparatus used in the NBL Titrimetric Method of Determining Uranium are described in a previous report.²

Technetium Stock Solution

An aqueous solution of NH_4TcO_4 , 5 mg Tc/ml.

Procedure

Transfer weighed aliquants of a standard solution, each containing approximately 100 mg of uranium, to 400-ml beakers. Add appropriate amounts of technetium to each aliquant, adjust volume to 15 ml and titrate.²

RESULTS AND DISCUSSION

Interference Effects

Results obtained from the analysis of uranium standards to which technetium was added are summarized in Table I. Relative errors are also listed. These errors show that Tc must be removed from samples prior to analysis.

TABLE I
EFFECT OF TECHNETIUM ON THE DETERMINATION
OF 100 mg OF URANIUM

<u>Uranium Added, mg</u>	<u>Technetium Added, mg</u>	<u>Uranium Found, mg</u>	<u>Relative Error, %^a</u>
104.035	15	84.944	-18.35
104.096	15	88.630	-14.86
109.213	15	80.136	-26.62
105.484	10	91.195	-13.55
103.545	10	92.797	-10.38
112.060	5	111.485	- 0.51
113.930	5	109.370	- 4.00
113.416	5	111.197	- 1.96
112.454	5	111.036	- 1.26
105.802	1	104.177	- 1.63

a. Relative error, % = $\frac{(U \text{ found} - U \text{ in standard})}{U \text{ in Standard}} \times 100$

Elimination of Interference

Technetium can be removed from aqueous solution by distillation of Tc(VII) from perchloric or sulfuric acid.³ Therefore, standards containing technetium were fumed in various mixtures of H₂SO₄, HClO₄ or H₂SO₄ and H₂O₂ prior to titration. Data in Table II show that simple fuming was not effective in removing all of the technetium from uranium samples.

TABLE II

RESULTS OF URANIUM DETERMINATIONS AFTER FUMING^a
STRONGLY WITH SULFURIC AND PERCHLORIC ACIDS

Uranium Added, mg	Uranium Found, mg	Reagents and Acid Added, ml	Technetium Added, mg	Relative Error, % ^b
108.021	107.895	0	0	-0.12
105.052	105.010	0	0	-0.04
113.564	113.544	0	0	-0.02
117.438	117.415	0	0	+0.02
111.485	111.519	0	0	+0.03
104.437	101.645	2 ml H ₂ SO ₄ , 5 ml HClO ₄	15	-2.67
103.648	103.279	" "	15	-0.36
104.834	103.760	2 ml H ₂ SO ₄ , 10 ml HClO ₄	15	-1.02
104.635	103.984	" "	15	-0.62
104.707	104.049	4 ml H ₂ SO ₄ , 5 ml HClO ₄	15	-0.63
104.967	104.337	9 ml H ₂ SO ₄ , 10 ml HClO ₄	15	-0.60
*105.241	104.432	5 ml H ₂ SO ₄ , 2 ml H ₂ O ₂	15	-0.77
*112.059	107.566	5 ml H ₂ SO ₄ , 0.25 ml H ₂ O ₂	15	-4.01
*113.769	109.334	" "	15	-3.90
*112.768	112.001	" "	15	-0.68
*112.128	111.487	" "	15	-0.57

* Tall form 400-ml beakers used with speedy vaps.

a. Fumed to near dryness

b. Relative error, % = $\frac{(U \text{ found} - U \text{ in standard})}{U \text{ in standard}} \times 100$

In another series of tests more drastic steps were taken to volatilize all of the technetium. The samples were fumed completely to dryness and the walls of the beakers were flamed with a blast burner to remove any traces of technetium which may have condensed during the fuming step. Tall-form beakers were substituted for the shorter 400-ml size to reduce any possible loss of uranium by spattering. Results for titration of samples treated in this manner are shown in Table III. These data show that all technetium was volatilized at higher temperatures by the flaming technique; all results were within the normal range of accuracy for the NBL method.

TABLE III

URANIUM DETERMINATIONS AFTER FUMING TO DRYNESS WITH
PERCHLORIC AND SULFURIC ACIDS AND A STRONG FLAMING
OF BEAKER WALLS WITH A BLAST BURNER

Uranium Added, mg	Acid Added, ml	Technetium Added, mg	Uranium Found, mg	Relative Error, % ^a
111.485	0	0	111.519	+0.03
116.371	5 ml H ₂ SO ₄ , 2 ml HClO ₄	15	116.372	+0.001
116.338	" "	15	116.436	+0.08
114.211	" "	15	114.251	+0.04
116.698	" "	15	116.693	-0.004
110.909	" "	15	110.941	+0.03
111.103	" "	15	111.134	+0.03

a. Relative Error, % = $\frac{(U \text{ found} - U \text{ in standard})}{U \text{ in standard}} \times 100$

CONCLUSION

Experiments have shown that Tc must be removed from uranium samples prior to titration. Removal is effected by fuming the samples to complete dryness from a mixture of H₂SO₄ and HClO₄, followed by flaming of the walls of beakers containing the samples.

In the routine application of the volatilization technique, conventional distillation procedures may be preferred.

No attempt was made in this work to study the interference mechanism of Tc. Such work may be undertaken in the future.

ACKNOWLEDGMENT

NBL is grateful for the participation of ORNL in this work.

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2. NBL-272, Appendix (A) (October 1974), p. 113.
3. Boyd, G. E., J. Chem. Ed., 36, (1959), p. 11.

THE EFFECT OF HIGH ALPHA ACTIVITY ON THE NEW BRUNSWICK
LABORATORY TITRIMETRIC METHOD OF DETERMINING URANIUM
- A JOINT EFFORT WITH OAK RIDGE NATIONAL LABORATORY

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Future requirements for on-line assay of HTGR recycle fuel will involve the analysis of uranium samples containing significant quantities of U-232. Essentially all of the alpha decay energy will be deposited, via secondary electrons, in the analyte during the chemical analysis of such samples. The resultant radiation damage could adversely influence the NBL titrimetric method. Therefore this experiment was designed to explore the effects of high density radiation on the accuracy of the uranium measurements.

Best estimates indicate that HTGR recycle fuel will contain about 1000 $\mu\text{g/g}$ of U-232. Thus, a typical 100-mg sample of uranium could contain 100 μg of U-232, equivalent to 2.08 millicuries of high energy alpha activity. Since uranium assay standards containing U-232 are not available, a substitute alpha particle source was selected which could be added to uranium standards without changing the uranium content. Curium-244 which has a specific activity about four times that of U-232 and which emits more energetic alpha particles proved to be an excellent substitute. The energy contribution from the decay of U-233 in the recycle fuel is less than 0.01% and is therefore disregarded.

Reagents and Apparatus

The reagents and apparatus used in the titrimetric method are described in a previous report.¹

Uranium Standards

Nitric-sulfuric acid solution prepared from NBL dingot uranium metal, ~10 mg U/g.

Curium Spike Solution

Curium-244, ~1 millicurie/ml in nitric acid.

Procedure

Transfer weighed aliquants of uranium standard solution, each containing approximately 100 mg of uranium to 400-ml beakers. Add appropriate amounts of the Cm-244 spike solution, adjust the volume to 15 ml, and titrate in accordance with the basic titrimetric method. Repeat, using 10 mg of uranium in the standard solution.

RESULTS AND DISCUSSION

The accuracy of uranium measurements made on 100-mg standards spiked with as much as 4 millicuries of Cm-244 was not affected by the presence of high density alpha radiation. Results are summarized in Table I.

TABLE I
DETERMINATION OF URANIUM IN THE PRESENCE OF
HIGH DENSITY ALPHA RADIATION

Amount of Uranium in Standard,mg	Millicuries of Cm-244	Equivalent U-232 Concentration,µg/g	Uranium Found,mg	Relative Error, % ^a
111.947	2	1,000	112.162	+ 0.19
112.421	2	1,000	112.419	- 0.002
113.056	2	1,000	113.030	- 0.02
110.753	2	1,000	110.812	+ 0.05
111.723	4	2,000	111.744	+ 0.02
11.774	2	10,000	11.730	- 0.37
11.377	2	10,000	11.412	+ 0.31
11.367	0	0	11.412	+ 0.40

a. Relative Error, % = $\frac{(U \text{ found} - U \text{ in standard})}{U \text{ in standard}} \times 100$

Although restricted working conditions prevented the attainment of the usual high precision and accuracy typical of measurements at the 10-mg level, results in Table I show that a concentration of U-232 as high as 10,000 ppm in a 10-mg uranium does not effect the accuracy of the NBL titrimetric method.

ACKNOWLEDGMENT

NBL is grateful for the participation of ORNL in this work.

REFERENCE

1. NBL-272, Appendix (A) (October 1974), p. 113.

THE DETERMINATION OF URANIUM IN FISSION-URANIUM ALLOY AND IN FISSION DROSS

L. Z. Bodnar

Fission alloy contains 95% U, 2.44% Mo, 1.94% Ru, 0.28% Rh, 0.19% Pd and lesser amounts of Zr, Nb, and Si; dross material may vary in composition. Fission-uranium alloy and fission dross contain several elements which normally interfere in the determination of uranium. The assay of these materials requires special dissolution techniques and specified procedures to eliminate potential chemical interferences arising from the presence of $\text{Mo} + \text{NO}_3^-$,¹ Ru,² and Cl^- ² in sample solutions. A simple pretreatment of sample solutions eliminates these interferences and allows the application of the NBL titrimetric method for the determination of uranium. This report discusses and compares several of these techniques.

EXPERIMENTAL

Reagents and Apparatus

Uranium Standards prepared from NBL dingot uranium metal.

Stock Solutions of Mo, Ru, Rh and Pd.

6N Sodium Hydroxide.

5% Sodium Hypochlorite.

30% Tributyl Phosphate (TBP) in Carbon Tetrachloride.

Other reagents and apparatus for use in the NBL titrimetric procedure are described elsewhere.³

Procedure

Dissolution of Fission Alloy⁴

Wash fuel pins in water and allow to dry in air. Weigh 1-2 g fuel pin to the nearest 0.0001 g. Place the sample in a 125-ml Erlenmeyer flask, add about 5 ml of water and heat to boiling. Remove the flask from the heat and add 25 ml of 4HCl:1 HNO₃ aqua regia. Allow the initial reaction to subside, then boil contents of the flask for 10 min. Cool the flask; quantitatively transfer contents of flask, including any solid material, to a 50-ml centrifuge cone and centrifuge for 10 min at a speed of about 3200 rpm. Decant the supernate to a clean, dry, preweighed bottle. Add 1 ml of 6N NaOH and 5 ml of 5% NaOCl to the residue in the centrifuge cone. Heat the contents of the cone in a boiling water bath for 10 min. Remove the cone and allow it to cool. Acidify the solution in the cone by dropwise addition of concentrated HCl and transfer the mixture to the main sample solution. Allow the solu-

tion to cool to room temperature, make up to desired volume with 1N HCl and mix well. Weigh the sample bottle and contents and calculate the grams of sample per gram of solution. Transfer immediately weighed sample aliquants containing about 100 mg of U to 400-ml beakers. Continue with treatment of sample aliquant when convenient as described below.

Dissolution of Fissium Dross

Weigh 1-2 g of the dross material into a 150-ml beaker. Proceed exactly as directed for the dissolution of the alloy up to the point at which the residue is treated with 1 ml of 6N NaOH and 5 ml of 5% NaOCl. Heat the contents of the centrifuge cone in the boiling water bath for 10 min. Cool the mixture and acidify by dropwise addition of HCl. Again, centrifuge the cone for 10 min at 3200 rpm. Decant the supernate into the bottle containing the main sample solution. Wash the remaining residue twice with 15 ml of water and transfer washings to main sample solution. Quantitatively transfer the residue to a 125-ml platinum dish with water. Add 5-10 ml of HF and a few drops of H_2SO_4 to the dish and evaporate to dryness on a steam bath to expel silica. Transfer, quantitatively, the remaining residue with water into a zirconium crucible and evaporate the water. Add about 1 g of NaOH to the dried residue and fuse the mixture over a Meker burner. When a clear melt is obtained, cool the crucible and dissolve the fusion cake in warm water. Acidify the solution with HCl and add it to the main sample solution. Weigh the sample solution, calculate the grams of sample per gram of solution, and weigh aliquants containing about 100 mg of uranium into titration beakers immediately. Continue with treatment of sample aliquant when convenient as described below.

Treatment of Sample Aliquants

Add 5-ml $HClO_4$ to the sample aliquant contained in a 400-ml beaker. Evaporate the solution to strong fumes of $HClO_4$ and continue heating until the purple color of H_2RuO_4 disappears and the color of the solution remains light yellow, indicating that all of the Ru has been volatilized. Continue heating until less than 4 ml of $HClO_4$ remains.⁵ (The fuming step also volatilizes chlorides and nitrates.) Cool the sample and adjust the volume to 12-15 ml with water. Titrate the sample using the NBL titrimetric method.

Preparation and Treatment of Synthetic Fission-Uranium Standards

Weigh an aliquant of the uranium standard solution containing 95-100 mg of U into a 400-ml beaker. Add 2.5 mg Mo, 2.0-mg Ru, 0.3-mg Rh, 0.2-mg Pd, 25 ml of aqua regia, 1-ml 6N NaOH and 5 ml of NaOCl. Evaporate the mixture nearly to dryness on a steam bath, cool, add 5-ml $HClO_4$ and continue as described under Treatment of Sample Aliquants.

RESULTS AND DISCUSSION

Previous reports on the titrimetric method of determining uranium have discussed the interferences of Mo, Ru, Pd and Cl^- . All of these substances are present in sample solutions of fissium-uranium alloy or dross material. Mo in the presence of nitrates causes premature oxidation of the Fe(II) reagent thereby causing the method to fail. Reduced species of Ru survive the oxidation step of the procedure and are subsequently titrated by the dichromate titrant, thereby leading to high results. Chloride interference is complex and involves poisoning of the platinum electrode. Pd is not present in quantities sufficient to cause significant error. The other constituents of fissium-uranium alloy do not interfere.

Five synthetic standards were prepared as described in "Preparation of Synthetic Fissium Standards." These standards, containing aqua regia, NaOH and NaOCl were fumed with 5 ml of HClO_4 to eliminate nitrates, chlorides and Ru as described under Treatment of Sample Aliquants and then titrated in the usual manner. Results are shown in Table I.

TABLE I
ANALYSIS OF SYNTHETIC FISSIUM STANDARDS AFTER
FUMING IN PERCHLORIC ACID

<u>Amount of U Added, mg</u>	<u>Amount of U Found, mg</u>	<u>Relative Error, %</u>
95.759	95.751	- 0.01
95.569	95.526	- 0.04
95.518	95.526	+ 0.01
95.659	95.687	+ 0.03
95.227	95.238	+ 0.01

These results, typical of those obtained by titrating pure uranium standards, indicated that the fuming technique is effective in eliminating all interferences.

A limited number of fissium alloy samples consisting of small pieces of fuel pins from the same melt were analyzed in a manner similar to that described for synthetic standards, but with some slight variations. Samples 1 and 2 were dissolved according to the procedure, including the residue treatment, as described. One aliquant from each was treated as described in the procedure and titrated. A second aliquant from each of these sample solutions was evaporated to dryness and then dissolved in 5N HNO_3 . Uranium was extracted into 30% TBP in CCl_4 and titrated directly. All results for samples 1 and 2 are in excellent agreement and are shown in Table II.

Samples 3 and 4 were dissolved according to the procedure described for alloy. However, the residues from these dissolutions were not separated and dissolved. Instead, the solutions were diluted directly to an appropriate volume and weighed. Two aliquants were then taken from each sample solution after thorough mixing to stir up the residue. One aliquant from each sample was fumed with perchloric acid and titrated in the usual manner. The second aliquants from samples 3 and 4 were evaporated to dryness and then dissolved in 25 ml of 5N HNO₃. The uranium contained in these samples was extracted into 30% TBP in CCl₄ and the organic phase titrated directly. These results for samples 3 and 4 are in good agreement.

Results for samples 1 and 2 are slightly higher than results for samples 3 and 4. Although the difference (0.07%) is not large and the amount of data are limited, the complete workup of any residue from sample dissolution appears to be essential to accurate analysis.

TABLE II
ANALYSIS OF FISSION-URANIUM ALLOY

Sample No.	Residue Treatment	Results (% U)	
		Aliquant Fumed in HClO ₄	Interferences Separated by TBP Extraction
1	Yes	94.630	94.632
2	Yes	94.653	94.662
3	No	94.583	94.567
4	No	94.551	94.580

Replicate analyses were performed on five subsamples taken from a ground, blended sample of fission dross. Results are shown in Table III. Three of these subsamples were dissolved and analyzed as prescribed in the procedure for fission dross. In the last two of the subsamples the insoluble residue remaining after the NaOH-NaOCl-HCl treatment was not dissolved. In one of these two samples the residue was separated by centrifugation, the solution was analyzed in the normal manner, and the residue was analyzed by spark source mass spectrometry. In the case of the other subsample the residue was dispersed in the main sample solution which was then aliquanted and analyzed as described in the procedure.

Results obtained for samples 4 and 5 again serve to point out that complete dissolution of the all residues is essential. The analysis of sample 4 from which the residue was separated yielded low results (relative to 1, 2 and 3) indicating that the residue may have contained uranium. Results from the analysis of sample 5 were high. This indicates that the residue may have contained small amounts of Ru and that the fuming process to volatilize Ru may not have been effective. However, spark source mass spectrometric analysis, Table IV, showed that the major constituent of the residue was Si. No uranium was observed and only a small amount of Ru. The amounts of other potentially interfering elements present in the residue do not account for the differences in the

results due to the presence or absence of the residue in samples titrated. Although the procedures described are probably satisfactory for the analysis of fission-uranium alloy and dross material, additional verification of accuracy and precision is planned and the role of the residue will be investigated.

TABLE III
ANALYSIS OF FISSION DROSS

<u>Sample No.</u>	<u>Size of Sub-Sample, g</u>	<u>Assay Value (% U)</u>
1	1	79.30, 79.31, 79.31
2	2	79.31, 79.33, 79.31
3	1	79.33, 79.34, 79.33
4 ^a	1	78.58, 78.59
5 ^b	1	79.91, 79.90

a. Residue separated from sample.

b. Residue dispersed in sample.

TABLE IV
SPARK SOURCE MASS SPECTROMETRY - SEMIQUANTITATIVE ANALYSIS
OF RESIDUE FROM THE DISSOLUTION OF FISSION DROSS

<u>Element</u>	<u>*Normalized Concentration, %</u>	<u>Element</u>	<u>*Normalized Concentration, %</u>
Si	77	Zn	0.5
Rh	8	Pd	0.4
K	4	Cu	0.4
Na	2	Ni	0.4
Al	1	Sn	0.3
Fe	1	Zr	0.3
Ru	0.8	P	0.3
Ag	0.7	Mo	0.2
Cu	0.6	Mg	0.04
Sb	0.5	In	0.02
Nb	0.5	Cs	0.02
		U	<0.01

* Excluding C, O, N, H, He and Li.

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DETERMINATION OF URANIUM FOLLOWING REDUCTION WITH
IRON(II) IN PHOSPHORIC ACID UTILIZING AMPEROMETRIC
END-POINT DETECTION

K. Lewis

The use of amperometric end-point detection was previously shown¹ to be applicable to the Davies-Gray procedure for the determination of 1- to 5-mg amounts of uranium with an accuracy and precision of 0.1%. The procedure adopted for the amperometric titration required a 5-min waiting period after the final dilution step with distilled water. The elimination of the waiting period was considered desirable and the present work was carried out to obtain a modification of the procedure leading to this result.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus are the same as those used previously¹ with the addition of the following titrant:

Ferrous Ammonium Sulfate. ~0.025 meq/gm in 1N H₂SO₄.

Procedure

Standardization of Ferrous Titrant. Place a magnetic stirring bar in the cell. Using pipets, add 0.5 ml of sulfamic acid and 3 ml of H₃PO₄ and start the stirrer at a moderate rate. Carefully pipet into the stirred solution 0.5 ml of ferrous sulfate solution and mix for 30 sec. Wash down the sides of the cell with 1 ml of HNO₃-molybdate reagent. (A dark colored solution forms and on continued stirring the color fades and disappears.) Wait 3 min after the color disappears and add 25 ml of distilled H₂O. Put the cell cap containing the electrodes in place, increase the stirring rate to create a mild vortex and connect the electrode leads. Using the working electrode as a potentiometric indicator, read the potential; the blank solution should have a value of +0.6V vs SCE. Weigh the K₂Cr₂O₇ weight buret; add K₂Cr₂O₇ until the potential reaches +0.7V vs SCE and about 1 g of K₂Cr₂O₇ solution has been added. Switch to potentiostatic control applying +0.8V vs SCE to the Pt working electrode. Wait 1.5 to 2 min to obtain a steady low background current, and while waiting weigh both the K₂Cr₂O₇ weight buret and the Fe(II) weight buret. Add Fe(II) titrant carefully until a steady current of 1 to 2 μ a is obtained; record the weight and the current. Add more Fe(II) titrant until a significant change in current is obtained and again record the weight and the steady current.

Calculations

By preliminary measurements, verify that a linear relationship exists between current, up to 10 μ a, and the amount of Fe(II) solution added. Then determine a standardization ratio between the Fe(II) and $K_2Cr_2O_7$ from the weight of $K_2Cr_2O_7$ solution taken and the weight of Fe(II) titrant required to reach the end point. Obtain the latter value by calculation, using the two sets of current-weight readings and the background current on addition of the Fe(II) titrant.

Determination of Uranium. The procedure is the same as that for the standardization with the exception that after dilution the uranium solution will have a potential of about +0.4V vs SCE. Add $K_2Cr_2O_7$ carefully until a potential of +0.7V vs SCE is obtained which indicates an excess is present. Continue the titration as in the standardization.

The calculations for the determination of uranium are the same as in the standardization except the final weight of Fe(II) titrant determined is multiplied by the standardization ratio to obtain the amount of excess $K_2Cr_2O_7$ added. This excess quantity is subtracted from the total amount of $K_2Cr_2O_7$ solution added, to determine the quantity of $K_2Cr_2O_7$ equivalent to the uranium present.

RESULTS AND DISCUSSION

The use of amperometric end-point detection for the determination of uranium utilizing the Davies-Gray reagent additions was examined and described in the previous annual report.¹ It was noted in reference (1) and in a report by Cherry² on biamperometric detection that a quantity of Fe(II) equivalent to the uranium in the sample is formed by a reaction between the excess Fe(III) present and U(IV) following the dilution step. The Fe(II) produced by this reaction is titrated with $K_2Cr_2O_7$. Techniques were developed in the previous work¹ allowing precise and accurate determinations to be carried out on 1- and 5-mg amounts of uranium using amperometry at a stationary Pt electrode in stirred solution. The reaction between Fe(III) and U(IV) is slow under the titration conditions, and thus a 5-min waiting period was found necessary prior to titration for the reaction to approach completion. The present work was aimed at developing a technique for eliminating the waiting period.

Four alternative means of accelerating the Fe(III)/U(IV) reaction were considered. First, a previously developed controlled-potential coulometric method³ based on the Davies-Gray procedure successfully used heated diluent to speed up the reaction. Since amperometric measurements are temperature dependent, this method would be cumbersome because it would require thermostatic control of the cell. Second, the use of a Fe(III) diluent which was also investigated in the prior coulometric work would accelerate the reaction, but large blanks associated with a reductant in the Fe(III) reagent caused problems. This method was therefore not attempted. Third, the addition of V(IV) which is used in the NBL titrimetric procedure to catalyze the final reaction was investigated. However, the presence of vanadyl sulfate resulted in variable background currents which lead to variable results. The

fourth method, involving the addition of a known excess of $K_2Cr_2O_7$ and the back-titration of the excess with a standard ferrous solution, was successfully adopted.

Table I shows that precise and accurate results are obtained on 1- and 5-mg quantities of uranium using the back titration procedure.

TABLE I
DETERMINATION OF URANIUM BY AMPEROMETRIC BACK TITRATION

<u>Amount of Uranium, mg</u>	<u>Number of Analyses</u>	<u>Coefficient of Variation, %</u>	<u>Recovery, %</u>
5	25	0.08	100.01
1	8	0.09	100.02

The primary disadvantage of the procedure is the necessity for standardization of the Fe(II) titrant. Some initial work has been done attempting to use electrogeneration of Fe(II) to avoid the need for standardization. Known amounts of $K_2Cr_2O_7$ have been titrated by electrogeneration in a blank solution using a Fe(III) diluent. Precise but low results have been obtained, so further work is being done to improve the accuracy.

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DETERMINATION OF URANIUM IN HARD-TO-DISSOLVE RESIDUES BY
X-RAY FLUORESCENCE

A. J. Busch and H. G. Yuster

Solid wastes and residues, such as calcined ashes, containing concentrations of uranium on the order of 0.1-5% often require an inordinate amount of time to be chemically analyzed. The dissolution of these complex inert materials and conversion to solutions suitable for analysis are tedious and time consuming. The analysis of these materials by X-ray fluorescence offers time-saving and economy in the assay of these difficult-to-dissolve samples.

A technique currently under investigation utilizes lithium tetraborate as a major component of a flux which produces a homogeneous glassy melt at 1100°C , with most solid samples, that can be cast to form a pellet suitable for fluorescence analysis. The flux to sample ratio is adjusted to eliminate most matrix effects which may complicate the interpretation of the results. A preliminary procedure is reported here for the preparation, casting and measurement of uranium in fused disks.

EXPERIMENTAL

Materials and Apparatus

Standards, prepared by adding an analyzed pitchblende (approximately 50% U) to dunite, in varying amounts, with thorough homogenizing. Control standards made by the addition of varying amounts of uranium to a synthetic calcined ash matrix, consisting of 50% SiO_2 , 27% Al_2O_3 , 13% Fe_2O_3 , 5% Nb_2O_5 , 3% CaO , and 2% BaSO_4 .

Chemplex Flux III, a commercial product composed of 16% La_2O_3 , 37% LiCO_3 and 47% $\text{Li}_2\text{B}_4\text{O}_7$.

Sodium Chloride, analytical reagent.

Graphite Crucibles, 25 to 30 ml volume.

Casting Dishes, Pt + 5% Au (a non-wetting alloy).

Graphite Casting Blocks

Plastic Vials, polystyrene 30 ml and 60 ml capacity, with one 3/8" plastic ball.

Mix Mill, Spex Industries, Inc.

Muffle Furnaces. One operated at 550°C and one at 1100°C.

X-Ray Spectrograph, Norelco inverted optic, tungsten X-ray target tube operated at 50KVP and 40 ma in an air path, 220 cut oriented LiF analyzing crystal, NaI(Tl) crystal scintillation detector operated at 826 V, single channel pulse height analyzer adjusted to a base line of 1.25 V with a 3 V window width.

Fused Disk Preparation. Grind the sample to pass through a 40-mesh screen blend and split into two subsamples. Place each subsample (3-5 g) into a 30-ml plastic vial with one mixing ball and shake in the mixer mill for 5 min to insure homogeneity of the subsamples. Into a 60-ml vial, with one ball, place 8 g of Chemplex Flux III, 1.5 g of sample, and 1.5 g of NaCl. Shake the mixture for 5 min in the mixer mill. Transfer the blended mixture to a graphite crucible and place in the 550°C furnace for 5 min. Transfer to the 1100°C furnace and after 5 min remove the crucible, swirl the contents and return to the furnace. Place the casting block and casting dish into the 550°C furnace. After 10 min remove the casting block and dish and place the casting assembly on a transite plate. Immediately remove the crucible from its furnace and pour the melt into the casting dish. Allow the entire assembly to cool to room temperature and gently dislodge the solidified disk from the dish.

Measurement. Place the disk, smooth side down, in the X-ray specimen holder. Count the sample for 100 sec at each of the following angles: U-L α peak at 37.29° (2 θ) and the background on both sides of the uranium peak at 36.30° and 41.30°. Calculate the net U-L α count by subtracting the weighted background equal to 0.7 of the 36.30° intensity plus 0.3 of the 41.30° intensity. Determine the uranium concentration in samples from the equation for the calibration curve.

Preparation of the Calibration Curve. Treat the standard samples of uranium in the same manner. Measure at least 5 standards at each of several levels representing a concentration range of 0-5%.

RESULTS AND DISCUSSION

Linear least squares analysis of the data shown in Table I yielded the constants for a calibration equation such that

$$C = 0.000823x - 0.0306$$

where: C = concentration in percent of normal uranium

x = net counts per sec.

TABLE I

DATA USED FOR CALIBRATION EQUATION

<u>Standard</u>	<u>Normal Uranium, %</u>	<u>X</u> <u>(Net Counts/Sec)</u>
NBL-76	0.01	21
NBL-75	0.05	79
NBL-74A	0.10	155
CG-1	0.49	596
CG-2	0.95	1310
NBL 42-3	1.07	1373
CG-3	1.94	2344
NBL 42-2	1.99	2542
NBL 42-1	4.04	4936

Six calcined ash samples, previously assayed by chemical methods, were analyzed in duplicate by the method described. In each case it was necessary to use isotopic data for conversion of the normal to the enriched uranium value. Results are shown in Table II.

TABLE II

X-RAY FLUORESCENCE MEASUREMENTS OF URANIUM CONCENTRATION
WEIGHT PER CENT COMPARED TO CHEMICAL RESULTS

<u>Sample</u> <u>No.</u>	<u>X-Ray</u>			<u>Chemical</u>
	<u>Cut a</u>	<u>Cut b</u>	<u>Average</u>	
1	0.42	0.38	0.40	0.43
2	0.62	0.69	0.66	0.67
3	0.80	0.79	0.80	0.80
4	0.99	0.98	0.98	1.00
5	1.48	1.47	1.48	1.48
6	2.41	2.42	2.42	2.42

The main purpose of this study was to establish a base upon which to study the effectiveness of different flux compositions and sample to flux ratios. Preliminary studies showed that the procedures used here were effective in producing homogeneous glassy melts which did not crack upon cooling and which did not degrade on standing. Although glassy melts were produced with most types of calcined-ash samples the flux composition was not suitable for samples containing significant quantities of silicon carbide. Future studies will be directed to the development of a more universal flux mixture and optimum sample to flux ratio leading to an improvement of accuracy and precision.

THE DETERMINATION OF URANIUM IN SCRAP MATERIALS BY
ISOTOPE DILUTION MASS SPECTROMETRY

A. W. Wenzel, J. R. Weiss, V. E. Connolly,
E. L. Callis and C. E. Pietri

The uranium content in low-grade uranium scrap material (0.5-1.5% U) has usually been determined by the NBL titrimetric method.¹ An alternative method, isotope dilution mass spectrometry (IDMS),² was considered and evaluated. Calcined ash samples containing 93% ²³⁵U were spiked with "normal" uranium tracer either before or after dissolution and the spiked uranium was separated from interfering materials. The separated uranium was determined by thermal emission mass spectrometry.

EXPERIMENTAL

Reagents and Apparatus

Uranium Tracer Solution. A solution containing 1 mg U/ml prepared from NBS SRM 960 normal uranium metal.

Thenoyltrifluoroacetone (TTA) in Hexone. 0.5M.

Resin. Dowex 1-X2, 50-100 mesh, chloride form.

Crucibles. Vycor glass (30 and 50 ml) and platinum (15 ml).

Ion-Exchange Columns. Polypropylene, Bio-Rad Catalog No. 7311110.

Mass Spectrometer. Nuclide Corp., 12" 60° with triple filament thermal ionization source.

Procedure

Spiking Procedure A: Weigh accurately a 0.5- to 2-g sample of calcined ash (93% ²³⁵U) containing about 1-10 mg uranium into a vycor crucible. Add, by weight, an aliquot of tracer solution containing an amount of uranium approximately equivalent to the uranium content of the sample. Mix with a platinum rod, rinse the rod with water, dry the mixture at 110°C, and then heat at 600°C in a furnace for 4 hr. Fuse the sample with NaHSO₄.³ (An alternative method of fusion using Na₂CO₃-NaNO₃ flux may be feasible for the dissolution of these samples.¹) Dissolve the fusion cake with water, filter, add 10 ml of HF to the filtrate plus 0.5 ml of water, 2 drops of HNO₃, 3 drops of H₂SO₄, and evaporate to dryness. Fuse any remaining residue with Na₂CO₃ in a platinum crucible.³ Dissolve the cake in 50 ml of 1:1 H₂SO₄ and filter. (Determine the uranium content of any remaining residue by gamma spectrometry.

The residue should contain less than 5% of the original uranium content of the sample.) Combine the filtrates from both fusions, precipitate the uranium with freshly prepared NH_4OH solution according to standard procedures,⁴ and filter. Dissolve the precipitate in 1:1 HCl so that the final volume does not exceed 40 ml. Transfer this solution to a 125-ml separatory funnel, add 20 ml of 0.5M TTA in hexone, cap, and shake for 2 min. Centrifuge, discard the organic phase and repeat the extraction. Transfer the aqueous phase to a beaker, evaporate to half its volume, add 10 ml of HCl , mix, and add the solution to a mini ion-exchange column containing Dowex-1 resin. Wash the column with 40 ml of HCl and elute the purified uranium with 20 ml of 0.1M HCl . Evaporate the solution to 2-ml volume, transfer to a 5-ml beaker with water, evaporate to dryness, add 2 ml of 8M HNO_3 , evaporate again, dissolve the residue in a few drops of water. Mount a portion of the solution on filaments for the mass spectrometric measurement.

Spiking Procedure B: Repeat the above procedure but add the tracer solution to the combined filtrates from the fusion steps. Mix the solution well and proceed to the NH_4OH precipitation step.

RESULTS AND DISCUSSION

Nine calcined ash scrap samples were analyzed by isotope dilution mass spectrometry (IDMS) and by conventional NBL titrimetry. The subsamples used for IDMS were taken using an improved sampling scheme. Four of the samples analyzed were spiked with the ^{238}U tracer prior to dissolution; the remaining samples were spiked following dissolution. The uranium was separated from interfering matrices using the above procedure. The results are shown in Table I. Also listed for comparison are the results from the analysis of samples from the same source of material by another laboratory using a titrimetric method similar to the NBL method.

The data show no significant differences (95% C.L.) between the two isotope dilution spiking techniques. Either technique, spiking prior or subsequent to sample dissolution, appears to be adequate. The agreement between the IDMS and titrimetry methods is satisfactory: there are no statistically significant differences between methods. The average difference between these two procedures for the nine samples is 1.1%. Both NBL methods compare favorably with the results from the other laboratory. Difficulty in sampling these heterogeneous scrap materials may be a major contributor to the poor precision obtained on these samples as compared to results on product-type materials.

The precision of the IDMS method appears to be better than the titrimetric method. However, this is probably due to improved mixing and sampling procedures used with the former technique.

The IDMS method for determining uranium in scrap samples has been shown to be an acceptable alternative method of analysis. The general agreement between the two independent methods, IDMS and titrimetry, adds confidence in the results obtained. Although the IDMS procedure is lengthy, in that several separations are required to purify the uranium prior to analysis, the method can be applied to samples containing less than 10 milligram amounts of uranium.

Furthermore, once the samples are spiked with tracer and equilibrated, quantitative separation (recovery) of uranium is not necessary.

TABLE I
COMPARISON OF URANIUM ASSAY RESULTS

Sample No.	IDMS		Titrimetry		R.D., %*	Other
	$\bar{x}$ (g U/g)	RSD, %	$\bar{x}$ (g U/g)	RSD, %		$\bar{x}$ (g U/g)
1	0.01077	0	0.01025	4.4	+ 5.1	0.01055
2	0.00942	1.1	0.00933	1.5	+ 1.0	0.00929
3	0.01093	2.9	0.01149	2.0	- 4.9	0.01101
4	0.00938	1.2	0.00939	4.0	- 0.1	0.00960
5	0.00974	3.5	0.00945	4.4	+ 3.1	0.00938
6	0.01057	1.0	0.01030	0.9	+ 2.6	0.01000
7	0.01090	2.0	0.01064	2.9	+ 2.4	0.01053
8	0.01363	1.5	0.01413	2.5	- 3.5	0.01383
9	0.01379	1.6	0.01323	7.8	+ 4.2	0.01346
n =	36		49			-
Av =		1.6		3.4	1.1	

*Relative difference between IDMS and titrimetry results:

$$\frac{\text{IDMS} - \text{titrimetry}}{\text{titrimetry}} \times 100$$

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COMPUTER SIMULATION OF HTGR FUEL MICROSPHERES
USING A MONTE-CARLO STATISTICAL APPROACH

C. E. Hedrick

Laboratory practice involving both in-house and interlaboratory comparison programs has indicated that attainment of precisions better than 0.3% (RSD) for the determination of uranium in replicate samples of HTGR fuel microspheres (TRISO) cannot be expected. A plausible explanation of the poor precision is not evident. Thus a significant effort has been devoted to the improvement of analytical measurements on this material.

One area of concern has been the sampling of fuel bead material and whether the complex physical structure of the individual fuel beads limits the homogeneity of gram-size samples with respect to an entire lot of the material. In order to investigate this question, a technique has been developed whereby any sample ranging in size from a single bead to multigram quantities of beads can be simulated and the theoretical uranium content (or that of any other constituent) calculated. Any number of such samples can be generated to represent random sampling of an entire lot of fuel beads. Thus the mean value for uranium content as well as the precision of the theoretical measurements can be calculated. These theoretical results can then be compared to the results from actual destructive analyses. The information obtained from these correlations can then be used as a guide in planning further improvements in analytical measurements; namely, whether poor precision can be explained in terms of the inherent homogeneity (or non-homogeneity) of the HTGR fuel material or in terms of analytical methodology or technique.

The simulation of fuel bead populations is based on a fuel microsphere model consisting of a core of U-Th carbide surrounded by four coatings consisting successively of carbon buffer, inner high density pyrocarbon, silicon carbide, and outer high density pyrocarbon. The model also includes the manufacturing specifications of composition, density and the physical dimensions of each of the structural entities.

The specifications assign mean values to each of the entities listed above as well as the deviations which can be expected. Practice has shown that deviations about the mean values exhibit a Gaussian distribution. Specifications also impose limits on the range of deviations which can be tolerated for each entity. Thus physical aspects of each structural entity may vary within limits; the sequential manner in which the various kernels and coatings are combined to form individual fuel beads results in a completely randomized population of beads relative to structure. The computa-

tional aspects of fuel bead simulation are based on modified Monte-Carlo statistics.

A preliminary validation of the simulation concept and the computational operations was made by comparing simulated weight loss on ignition of the outer pyrolytic carbon coat with results from an experiment in which individual fuel beads were ignited to measure actual weight loss. Although only 50 individual beads were utilized in each case the theoretical mean weight loss was 29.0 μg per bead and the actual mean weight loss for 50 beads was 27.4 μg . The mean weight of the 50 simulated beads was 110 μg and that for actual beads was 118 μg . The positive correlation of the results was excellent. In another validation test the mean theoretical uranium contents of random samples of 50,000 fuel beads (11 g) was established at $0.03404 \pm 0.06\%$ (RSD) g U/g as compared to destructive analysis results of $0.03342 \pm 0.18\%$ (RSD) g U/g.

Other general observations suggest that, as expected, precision improves with increased sample size. It was also noted that the magnitude of the deviations from mean values assigned to structural entities has only a minor effect on the precision of measurements.

Although the results of preliminary studies provided confidence in the application of the simulation concept, some of the computational program changes were indicated. Details of the studies reported here and of future work will be presented in a separate report scheduled for early in 1976.

A VOLUME-DEPENDENT COUNT CORRECTION FACTOR FOR
THE DELAYED NEUTRON ANALYSIS OF URANIUM-235

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

Delayed neutron analysis is frequently applied to the measurement of ^{235}U content of small samples that differ both in volume and fissile content. In such applications the accuracy of the measurement is critically affected by the self absorption of the material and to a lesser extent, the combined geometry of the sample and the source. Count correction factors which change with respect to changes in these variable parameters of self absorption and geometry may be derived to minimize the effect of these variables. For example, samples occupying the same vial volume, but having different fissile content will have different correction factors relative to samples with the same fissile content but occupying different volumes.

A polynomial equation of the form,

$$c = k_0 + k_1W + k_2H + k_3W^2 + k_4HW + k_5H^2 + k_6H^2W^2 \quad (1)$$

Where, c = total delayed neutron count, per mg ^{235}U ,

W = weight of the fissile material in the counting vial in mg, ^{235}U ,

H = height of the material in the counting vial in mm,

and k_0 through k_6 are constants,

was selected to represent the relationships among the critical factors and the observed delayed neutron count. This equation and the derived constants serve as the basis for determining count correction factors for all types of samples.

EXPERIMENTAL

Apparatus

Neutron Source. The neutron source contains 850 μg of ^{252}Cf ; the source assembly has been previously described.¹

Counting Equipment. The neutron counter consists of thirty He-3 detectors, 51-cm long, placed in three concentric circles around a well, 5 cm in diameter. The counting equipment has been previously described.¹

Sample/Standard Vials. Polyethylene, 16-mm o.d. x 50-mm high.

Materials

U₃O₈ (94% ²³⁵U).

MgCO₃, reagent grade.

Al₂O₃, reagent grade.

Procedure

Preparation and Treatment of Standards. Add 25 mg of ²³⁵U as U₃O₈ (94% ²³⁵U) to each of 7 counting vials. Add sufficient MgCO₃ or Al₂O₃ to adjust the total height of material in the vials 1 through 7 to approximately 5, 10, 15, 20, 30, 40 and 50 mm, respectively. Mix the contents of each vial thoroughly, tap and measure the height of the mixture to the nearest mm. Prepare similar mixtures containing 50, 250, 500 and 1000 mg of ²³⁵U.

Place each vial in the neutron source and activate each for 2 min. Remove the vial from the source and count delayed neutrons for 100 sec, starting 10 sec after removing the vial from the source.

RESULTS AND DISCUSSION

Counting data for all standards are shown in Table I and plotted in Figure 1.

The measured delayed neutron count per milligram of ²³⁵U and the height of the material in the vial may be substituted into equation (1) for each standard. Constants k₀ through k₆ may then be calculated by a multiple regression analysis using a least squares fit. These constants, shown in Table II, are subsequently used in calculating the count correction factors. Self-absorption, which is related to fissile content, and the height of the sample in the vials, which is associated with the geometry of the system, are inherent in the constants as calculated.

The basic concept for the estimation of a count correction factor for samples of different volumes and different fissile content involves the normalization of all counting data to a fixed height and specified ²³⁵U content. This normalization procedure involves the calculation of the count correction factor as represented by equation (2), using the derived constants:

$$C.F. = \frac{C_f}{C_m} = \frac{k_0 + Wk_1 + 50k_2 + W^2k_3 + 50Wk_4 + (50)^2k_5 + (50)^2W^2k_6}{k_0 + Wk_1 + Hk_2 + W^2k_3 + HWk_4 + H^2k_5 + H^2W^2k_6} \quad (2)$$

where, C_f = Calculated counts for a sample 50-mm high containing W mg of ²³⁵U,

TABLE I

DELAYED NEUTRON RESPONSE AS A FUNCTION OF
URANIUM-235 CONCENTRATION AND SAMPLE GEOMETRY

²³⁵ U Content, mg	Matrix, g	Total Height, mm	Delayed Neutron Response cts/mg ²³⁵ U
25	0.95 (Al ₂ O ₃)	5.0	311
	1.90	9.5	319
	2.85	14.0	325
	3.81	19.0	326
	5.70	29.0	336
	7.60	39.0	329
	9.50	47.0	330
50	0.95 (Al ₂ O ₃)	5.0	311
	0.30 (MgCO ₃)	12.5	309
	0.61	25.0	324
	0.91	34.0	329
	1.21	43.0	330
	1.52	47.0	323
250	0.86 (Al ₂ O ₃)	5.0	239
	1.70	9.5	260
	2.60	14.0	275
	3.40	17.5	283
	5.10	26.0	295
	6.80	38.5	301
	8.64	46.0	301
500	0.23 (MgCO ₃)	7.5	204
	0.34	11.5	223
	0.46	15.0	237
	0.69	21.0	253
	0.92	29.0	267
	1.15	37.5	276
	1.38	44.0	276
	1.59	47.5	279
1000	0.19 (MgCO ₃)	5.5	144
	0.38	11.5	174
	0.56	17.5	193
	0.75	22.0	204
	0.91	20.5	217
	0.99	31.5	223
	1.26	40.0	231
	1.47	44.0	233

FIGURE 1. VOLUME-DEPENDENT DELAYED NEUTRON RESPONSE.

C_m = calculated counts for a sample vial filled to a height H and containing W mg of ^{235}U ,

W = weight of ^{235}U in mg, present in a sample,

H = height in mm, of the sample.

TABLE II

CORRECTION FACTOR CONSTANTS FOR THE NBL CALIFORNIUM-252
THERMAL NEUTRON SOURCE CONFIGURATION

<u>Constant</u>	<u>Value</u>
k_0	$3.073 \times 10^2 \text{ mg}^{-1}$
k_1	$-3.064 \times 10^{-1} \text{ mg}^{-2}$
k_2	$1.968 \text{ mm}^{-1} \text{ mg}^{-1}$
k_3	$1.078 \times 10^{-4} \text{ mg}^{-3}$
k_4	$4.262 \times 10^{-3} \text{ mm}^{-1} \text{ mg}^{-2}$
k_5	$-3.153 \times 10^{-2} \text{ mm}^{-2} \text{ mg}^{-1}$
k_6	$-4.776 \times 10^{-8} \text{ mm}^{-2} \text{ mg}^{-3}$

Thus, the count correction factor, C.F., is the ratio of the counts that would be measured for a vial filled to a height of 50 mm to the counts that would be observed for a specific sample height and ^{235}U content.

For routine sample analysis the quantity of ^{235}U , W in equation (2), is unknown and is in fact the quantity being measured; however, the correct value can be derived from an iterative process based on the use of estimated values for ^{235}U content. The initial estimate for the amount of ^{235}U in a sample is best made from counting data in conjunction with the expression,²

$$C_u = A(1 - e^{Bx}) \quad (3)$$

where C_u = measured uncorrected count,

A = proportionality constant which includes neutron strength and the absolute detector efficiency,

B = non-linear self absorption coefficient related to the cross section,

and x = weight of ^{235}U involved.

The constants A and B may be determined by a linear least squares regression analysis using equation (3) and the uncorrected counting data for standard vials filled to a fixed height (50 mm in this case) and containing known amounts of ^{235}U . These standards may be those used to determine the constants k_0 - k_6 or any other

set of known standards meeting the requirements of height and concentration.

The estimated weight of ^{235}U determined from uncorrected counting data (Equation 3) is used to calculate an intermediate corrected count and an intermediate count correction factor (Equation 2). The intermediate correction factor is subsequently used in the iterative process to revise the weight estimate, x_w , as shown in equations below:

$$C_c = C.F. \times C_u = C.F. \times A(1 - e^{-Bx_w}), \quad (4)$$

where $x_w = \frac{\ln 1 - \frac{C_c}{C.F. \times A}}{B}$, the corrected weight of ^{235}U .

The iterative process is repeated until additional iterations fail to produce significant changes in the value for the correction factor, C.F. (Equation 2). Thus the values of both the correction factor and the weight of ^{235}U are established at convergence where $x_w = W$. In this work the value for the count correction factor converged to seven significant figures within 12 iterations. The correction factor for each particular sample may be determined in this manner.

Several samples of uranium scrap covering a wide range of uranium concentrations were analyzed by delayed neutron analysis, using the count correction factors as described above. Results are shown in Table III. The total uranium content of these samples was calculated by using the measured isotopic abundances in the sample.

TABLE III
ANALYSIS OF URANIUM SCRAP SAMPLES BY DELAYED
NEUTRON COUNTING

Sample No.	Height (mm)	Content (Corrected) mg U	Content (Uncorrected) mg U/g	Content (Corrected) mg U/g	Content by Chemical Analysis mg U/g
1	26.5	61.8	8.0	7.9	7.8
2	24.5	92.5	12.5	12.5	12.2
3	19.5	237	39.9	42.0	44.3
4	31.5	294	42.2	42.8	43.6
5	20.5	919	156	163	167

Results obtained by DNA are in good agreement with values obtained by chemical analysis, with an average difference of 2.3% between the methods.

In general, this count correction factor is small (1-2% as for samples 1-4) since most samples received for analysis are more than half full and contain less than 300 mg ^{235}U (less than 3% by weight). However, for samples of higher fissile content or small sample volumes the count correction factor (>2% as for sample No. 5) is important and cannot be ignored.

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AN EVALUATION OF THE NEW BRUNSWICK LABORATORY
12" 60° MASS SPECTROMETER USING A NATIONAL BUREAU
OF STANDARDS STYLE SYSTEM CALIBRATION

V. E. Connolly, E. L. Callis and A. W. Summers

The New Brunswick Laboratory (NBL) has been involved for many years in the isotopic analysis of uranium and other nuclear materials using thermal ionization techniques. In the routine analysis of uranium samples using rapid analysis techniques and "in-house" calibration methods, isotopic ratios are determined with accuracies of 0.2% (95% confidence level for a single determination).

This report deals with a study to demonstrate performance capabilities of the NBL instrumentation in non-routine situations using a National Bureau of Standards (NBS) calibration procedure.¹ This procedure involves the determination of the mass discrimination factor, or correction factor (CF), for a series of NBS uranium SRM's, covering $^{235}\text{U}/^{238}\text{U}$ ratios in the range of 0.05 to 20. This correction factor should be constant, within experimental error, over the entire range, if the measuring system is functioning properly and if experimental parameters such as sample loading, filament temperature and heating cycles are closely controlled as specified in the NBS calibration procedure.

Some modifications have been made in the NBS technique as applied here because of differences in design of the NBL and NBS mass spectrometer systems.

EXPERIMENTAL

Reagents and Apparatus

Isotopic Standards. NBS-SRM's U-050, U-100, U-150, U-200, U-350, U-500, U-750, U-800, U-850, U-900, U-930. Aqueous uranyl nitrate solution of each standard; U concentration, ~10 mg/ml.

Mass Spectrometer. Nuclide Associates, Model SU-3 (12" 60°), as modified by NBL.²⁻⁴

Pre-degassing Chambers consisting of filament heating assembly enclosed in evacuable bell jars.

Micro Optical Pyrometer.

Sample Loading Apparatus - Device which supplies 0 to 5A to the filament during loading to facilitate conversion of the sample to the yellow-orange oxide.

Procedure

Filament Temperature Calibration. Using the pre-degassing chamber, measure the temperature of the central and side filaments of several assemblies as a function of filament current. Plot the data and note the current reading to obtain a central filament temperature of 2150°C . Note the ^{187}Re emission during an analysis at the same condition. Perform the same type of measurement for both the conventional triple filament assemblies and disposable filament beads⁶ (see Figure 1).

Measurement. Load 50-60 μg of uranium onto each side filament of the conventional assemblies and 30-40 μg onto each side filament of the disposable beads while maintaining a current of 1.3A through the filaments. Evaporate the loadings to dryness and increase the filament current slowly to 1.9-2.1 A and continue heating until the characteristic yellow-orange oxide is formed.

Insert the filament assembly into the vacuum lock of the mass spectrometer. Pump for five min and insert the sample into the source. Degas for 5 min at a current of 3 A on the ionizing filament and 1 A on each side filament. Then increase the side filament current slowly to 2 A and hold for a few sec, then reduce current to 1 A. Increase the current through the ionizing filament to 4 A, and continue degassing for 15 min. Increase the ionizing filament current to 5.0 A (as determined in temperature calibration procedure) and fine adjust to give a ^{187}Re emission of 1.5×10^{-11} A. Then increase the temperature of one sample filament until an ion beam of about 3.0×10^{-11} A is obtained. Maintain this setting for 5 min then increase the temperature (filament current of ~2.5 A) until an ion intensity of 5 to 7×10^{-11} A is obtained. Adjust current as necessary to maintain this intensity for five min.

At this point begin measurements by magnet switching between peak tops allowing 30 sec for each peak top to be measured. Measure five peaks of each isotope to yield eight 235/238 ratios. Scan the mass range to establish base lines. Terminate measurements if instability, excessive rise or fall of intensity is noted or if more than 20 min are required to stabilize ion beam.

RESULTS AND DISCUSSION

The mass spectrometer used in this study is an NBL modified Nuclide Associates Model SU-3 of a 12" 60° design with an NBL designed vacuum lock.^{2,3} The ion source is a modified Dietz design⁴ with "Z" focusing operated at 14 kV and a slit width of about 0.14 mm. Filament power is supplied by a current regulated filament supply (Nuclide Corp.). A 100 l./sec ion pump is used on the source chamber and a 50 l./sec ion pump on the analyzer section.

The collector is a deep Faraday cup mounted behind an adjustable slit and a series of suppressor plates at a negative 90 V. The collector slit width is set at about 0.5 mm. Two vibrating reed electrometers (VRE) (Cary Model 31) in a master-slave operation and an expanded scale recorder of NBS design⁵ form the measuring circuit. The slave VRE monitors the ion beam falling on the adjustable slit

FIGURE 1. FILAMENT ASSEMBLIES
[Left Disposable Bead (1" Diameter), Right is Conventional Assembly]

while the master VRE measures the ion current on the Faraday cup. A 10^{11} ohm resistor was used in each VRE.

Calibration of the expanded scale circuit indicated that the electrometer range scales to be used (1V, 3V, 10V) were within 0.02% of nominal full scale values and there were no discernable differences in the expanded scale decade positions. Therefore no corrections were made for range scale or decade positions. A minimum deflection of 30% of full scale for each peak was used for all 235/238 ratios.

One of the most critical control parameters is filament temperatures. The 12" 60° instrument lacks a viewport to the ionization chamber; therefore, the correlation of filament current and filament temperature was performed in the pre-degassing chambers which are topped with bell jars. A plot of current vs. temperature was made on several central and side-filaments using a micro optical pyrometer. The temperature at 5.0A on the central filament was about 2150°C and the ^{187}Re emission at 5.0A in the instrument was about 1.5×10^{-11} A, which is in good agreement with NBS data.

In Table I are shown the results of replicate analyses of SRM U-500. Tables II and III are the system calibration runs made with disposable beads and conventional assemblies, respectively. All 95% confidence levels shown are for a single analysis.

Overall, the data taken with conventional assemblies are somewhat better than those obtained with the disposable beads. In general, the ion beam with conventional assemblies stabilizes more rapidly and has a lower rate of rise or fallout.

Data for conventional assemblies shown in Table III indicate that the present system is linear to within $\pm 0.05\%$, as indicated by the range of 0.10% in the correction factor determinations. The precision of an individual determination of $\pm 0.08\%$ (95% C.L.) compares favorably with NBS system calibration data.⁷ It should be noted that the precision values for individual runs in Tables II and III represent a worst case situation since all sources of error (namely: run to run variation, nonlinearity of the measurement system and uncertainties in the NBS certified values) contribute.

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TABLE I
DETERMINATION OF MASS BIAS

Disposable Beads			
Measured			
<u>SRM</u>	<u>Run</u>	<u>235/238 Ratio</u>	<u>C. F.</u>
U-500	1	1.00341	0.99630
	2	1.00326	0.99645
	3	1.00372	0.99599
	4	1.00380	0.99592
	5	1.00342	0.99629
	6	1.00371	0.99600
Average		1.00355	0.99616
RSD		<u>+0.022%</u>	
95% C.L.		<u>+0.056%</u>	

Conventional Assemblies			
U-500	1	1.00440	0.99532
	2	1.00417	0.99555
	3	1.00469	0.99503
	4	1.00431	0.99541
	5	1.00411	0.99561
	6	1.00390	0.99582
Average		1.00426	0.99546
RSD		<u>+0.027</u>	
95% C.L.		<u>+0.069</u>	

TABLE II

SYSTEM CALIBRATION WITH DISPOSABLE BEADS - 235/238 RATIOS

<u>SRM</u>	<u>NBS Value</u>	<u>Measured</u>	<u>C. F.</u>	<u>Average</u>	<u>C. F.</u>
U-050	0.05278	0.05298 0.05294	0.99622 0.99698	0.05296	0.99660
U-100	0.11360	0.11409 0.11396	0.99571 0.99684	0.11402	0.99632
U-150	0.18109	0.18174 0.18170	0.99642 0.99664	0.18172	0.99653
U-200	0.25126	0.25188 0.25178	0.99754 0.99793	0.25183	0.99774
U-350	0.5465	0.5484 0.5485	0.99654 0.99635	0.5485	0.99635
U-500	0.9997	1.0031 1.0035	0.99661 0.99621	1.0033	0.99641
U-750	3.166	3.180 3.178	0.99560 0.99622	3.179	0.99591
U-800	4.266	4.285 4.284	0.99557 0.99580	4.284	0.99580
U-850	6.148	6.174 6.169	0.99579 0.99660	6.172	0.99611
U-900	10.375	10.417 10.411	0.99597 0.99654	10.414	0.99626
U-930	17.349	17.414 17.417	0.99623 0.99610	17.415	0.99621
Average C. F.			0.99638		0.99639
Range			0.24%		0.19%
95% C. L.			$\pm 0.122\%$		

TABLE III

SYSTEM CALIBRATION WITH CONVENTIONAL ASSEMBLIES — 235/238 RATIOS

<u>SRM</u>	<u>NBS Value</u>	<u>Measured</u>	<u>C. F.</u>	<u>Average</u>	<u>C. F.</u>
U-050	0.05278	0.05302 0.05301	0.99547 0.99566	0.05301	0.99547
U-100	0.11360	0.11408 0.11406	0.99579 0.99597	0.11407	0.99588
U-150	0.18109	0.18183 0.18184	0.99593 0.99587	0.18184	0.99587
U-200	0.25126	0.25245 0.25233	0.99529 0.99576	0.25239	0.99552
U-350	0.5465	0.5487 0.5492	0.99599 0.99508	0.5490	0.99545
U-500	0.9997	1.0046 1.0048	0.99512 0.99492	1.0047	0.99502
U-750	3.166	3.179 3.181	0.99591 0.99528	3.180	0.99560
U-800	4.266	4.287 4.284	0.99510 0.99580	4.286	0.99533
U-850	6.148	6.173 6.177	0.99595 0.99531	6.175	0.99563
U-900	10.375	10.427 10.428	0.99501 0.99492	10.428	0.99492
U-930	17.349	17.427 17.434	0.99552 0.99512	17.430	0.99535
Average C.F.			0.99549		0.99546
Range			0.11%		0.10%
95% C.L.			<u>+0.080%</u>		

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THE EVALUATION OF THE LOS ALAMOS SCIENTIFIC LABORATORY BOMB
SAMPLE DISSOLUTION TECHNIQUE AND AUTOMATED EXTRACTION
SPECTROPHOTOMETER FOR URANIUM ASSAY

C. Hassell, Jr., J. S. Paller and C. E. Pietri

A system for the automated analysis of uranium samples, developed by the Los Alamos Scientific Laboratory (LASL), has been evaluated for ERDA and LASL at the New Brunswick Laboratory (NBL). The system consists of dissolution of the dry sample in a teflon-lined Parr bomb at 280°C for 12 hr using a HNO₃-HF medium, filtration of the sample, gamma counting of the residue to determine the U content, and assay of the filtrate for uranium by an automated extraction spectrophotometer (AES).¹ The uranium solution is manually loaded into precision-bore extraction tubes; the AES then automatically adds a salting solution containing tetrapropylammonium nitrate (TPAN) to complex the uranium, extracts the complex using 2-nitropropane, reads the absorbance of the organic layer with a narrow bandpass spectrophotometer, and gives a print-out of the absorbance values. A more detailed discussion of the instrument and its operation is given in a LASL report.²

Two evaluation programs of this system were conducted at NBL. The AES was studied using prepared uranium standard solutions in order to determine the precision and accuracy of the instrument under actual routine operating conditions. A second program was begun to determine the feasibility of using the complete dissolution/assay system as a means of determining uranium in difficult-to-dissolve scrap samples.

EXPERIMENTAL

Reagents

2.8M Al(NO₃)₃, 2N Acid-deficient, 0.025M (Pr)₄NOH. Place 1050 g Al(NO₃)₃·9H₂O in a 2-l. beaker and add water to a volume of 850 ml. Heat, and after dissolution add 135 ml NH₄OH. Stir until precipitate dissolves. Cool to <50°C, add 50 ml 10% tetrapropylammonium hydroxide (Pr)₄NOH (Eastman No. 6189) and stir until dissolved. Transfer to 1-l. volumetric flask and dilute to volume.

2-Nitropropane. Eastman No. 4680.

Saturated Al(NO₃)₃ Solution. Add approximately 200-ml water to about 450 g of Al(NO₃)₃·9H₂O, and mix on an automatic stirrer for approximately 8 hr. Decant the liquid portion and let stand overnight. If more crystals have formed, decant the liquid again.

Uranium Standard Solutions. Prepare from NBS SRM 960 uranium metal to give eight different concentration levels (approximately 1-, 2-, 4-, 5-, 6-, 7-, 10-, 12-mg U/0.5 ml solution).

Apparatus

Automated Extraction Spectrophotometer consisting of the following main subassemblies: a 24-position turntable with Geneva drive system, 3 hydraulic piston-type reagent dispensers, a magnetic stirrer, a filter spectrophotometer, a control mechanism for sequential operation, and electronic data converter and printer.

Glass Extraction Spectrophotometer Tubes. (See Figure 1.) Fabricated from precision-bore 0.750 ± 0.001 " i.d. tubing closed and rounded at the bottom and flared at the top to fit in holes in turntable. (Satisfactory results are not obtainable with tubes which do not comply with these specifications in full.)

Blue M model POM 146 C-1 oven with integral 12-hr timer.

Parr 347 Stainless Steel Dissolution Containers. (Parr Cat. No. 4746) (See Figure 2) equipped with a pressure relief hole, and 0.010" and 0.002" stainless steel rupture discs.

Teflon Dissolution Container Liners. Reuseable, with long-taper joint for good pressure sealing.

Procedure

Calibration Curve. Prepare a calibration equation for the spectrophotometer as follows: Accurately weigh four 0.5-ml aliquots of each of the 8 different standard solutions into extraction tubes. Add a teflon-coated stirring bar to the tubes, insert the tubes in the AES turntable and start the automatic operation in which the following operations are performed. The salting solution is dispensed into the tube to complex the uranium(VI), 2-nitropropane is dispensed to extract the complex, and the sample is stirred to effect the extraction. Saturated $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution is added to raise the organic phase above the level where aqueous droplets might adhere to the side of the tube. All reagents are dispensed from hydraulically driven piston-type dispensers. Absorbance is then read by a narrow bandpass spectrophotometer at the 452.5 nm peak and the associated valley, using a 45 W quartz iodine lamp as a light source and a 929 photodiode as a detector. The detector output is converted to binary code, corrected for dark current and accumulated for four readings at both the peak and the valley wavelengths. Averages of the two sets of readings are computed, and $\log_{10}$ of each average is calculated. $\log_{10}\text{peak}$ minus $\log_{10}\text{valley}$ is converted to binary coded decimal (BCD) form and printed as a four-digit number along with the previously stored filter pair designation and turntable position numbers. All readout operations and calculations are performed by a minicomputer, and a quadratic equation, $f(x) = A+Bx+Cx^2$, was fitted to the calibration data in which x = instrument readout, $f(x) = g U$; A, B, and C are coefficients of regression lines. A typical calibration curve from this equation is plotted in Figure 3.

Sample Analysis. Accurately weigh a 1-2 g calcined ash scrap sample containing 10-15 mg U into one of the teflon liners, add 6 ml HNO_3 and 0.5 ml HF, and insert the liner into a numbered stainless steel dissolution container. Place the container in the

FIGURE 1. PRECISION-BORE SPECTROPHOTOMETER TUBE.

FIGURE 2. PARR STAINLESS STEEL DISSOLUTION
CONTAINER WITH TEFLON LINER.

oven for 12 hours at 280°C. After dissolution, remove and dismantle the container, removing the teflon liner. Filter the partially dissolved sample through a Millipore system, using 8M-HNO₃ to wash the uranium into the filtrate, and water to wash the acid out of the residue. Dry the residue and place in a vial for gamma counting.

Weigh an aliquot of the filtrate or solution sample no larger than 4 ml into one of the specially fabricated glass extraction tubes, and take the sample to dryness by suspending over a hotplate. Redissolve with 0.5 ml 8M HNO₃, and insert the tube into the turntable, after adding a teflon-coated stirring bar. Start the automated system and continue according to the procedure used for the calibration curve above.

RESULTS AND DISCUSSION

The evaluation of the LASL bomb sample dissolution and automated extraction spectrophotometer (AES) analysis system consisted of three phases: (1) preliminary examination of instrument calibration and operation using uranium standards, (2) automated analysis of uranium standards under routine operating conditions, and (3) automated analysis of actual scrap samples using the bomb dissolution technique. The evaluation was performed using the recommended procedure.

The results from preliminary tests made on the AES, using four runs on each of eight different uranium concentration standards daily for twelve days, indicated major shifts in the calibration curve. Significantly poorer results than the data reported by LASL³ were noted between some standard levels and among replicates of several standards. Several exploratory steps were taken, some of which were recommended by LASL, including changing the photodiode, keeping the equipment turned on at all times, adding a voltage regulator to the line input, and replacing the glass extraction tubes with tubes of the specified dimensions. (In the latter instance, examination of the specially-fabricated tubes indicated that some from the first batch did not meet the design specifications required for reliable spectrophotometric measurements.) It is not known whether all of the above changes are needed for proper instrument operation at all locations but their use at NBL, at least in part, appears to have resulted in increased reliability.

The second part of the program, essentially a repeat of the first tests after making the noted instrumental modifications and generating a new calibration curve, produced significantly better results. The data from the 1- and 2-mg levels verified LASL observations that analysis in this range gives less reliable results than at the 3- to 12-mg levels. Using only the results from the 4- to 12-mg uranium levels, (NBL did not examine a 3-mg U level) the daily relative standard deviation (RSD) of the determined g U/g values varied from 0.12 to 0.24% (average 0.18%). Although the average mean of the relative difference of the determined uranium values from the prepared value of the standards was +0.13%, the daily mean relative differences ranged about 1% (-0.37 to +0.60%), Table I, column 2. The cause of these daily variations is not known. Figure 4 shows the 90% confidence intervals about the regression coefficients and indicates that the differences among

FIGURE 4. PER CENT CONFIDENCE LIMITS FOR THE QUADRATIC COEFFICIENTS OF REGRESSION.

the coefficients were statistically significant on some days. In order to reduce the magnitude of these differences, the same data were evaluated using a daily calibration curve generated from the first run of each standard level for that day. Treated in this manner, the daily mean relative differences for the 4- to 12-mg range varied from -0.23 to +0.08% (average -0.04%); the range of these differences was reduced from about 1% in the initial tests to 0.3%, Table I, column 3. The 1- and 2-mg levels were not homogeneous with the 4-12 mg range in regard to precision and accuracy using a quadratic equation fit of the data. A separate calibration using sufficient data at the 1- to 2-mg range would be advantageous in characterizing the performance at this level. Thus, these data would indicate that for the analysis of high-grade uranium materials the best results would be obtained by using the instrument in the 4-12 mg U range with daily calibration. For the assay of uranium in heterogeneous scrap at low uranium concentrations, the use of the 1- and 2-mg U levels with average uncertainties of <1% and <0.5% RSD, respectively, would be satisfactory. In routine operation a daily 6-point calibration curve would require about 1 hr. The end use of the AES would determine whether or not daily calibration is necessary or economically feasible. Table II shows the RSD observed in each level and day, and also gives a summary of the results for each concentration level and day. The data indicate the lower reliability of the 1- and 2-mg levels. LASL has successfully used a "daily verification" scheme (instead of daily calibration) in which standards are run daily to determine if the calibration curve is within control limits.²

Prior to beginning the sample analysis phase of this evaluation program, a series of standards were run to determine the effect of temperature on instrument stability. Four standards ranging from 4- to 10-mg uranium were analyzed on each of four different days at four different ambient temperatures. The results verify the observations made at LASL.² The data in Table III show that 18°C (the temperature at which the calibration curve was generated) gave the best results. This temperature dependence does not appear to be the cause of the daily shifts in instrument calibration encountered during the previous tests since the maximum temperature variation between days was $\pm 1^\circ\text{C}$ and shifts occurred when the temperature was constant.

In the final testing of the complete system with calcined ash scrap samples (bomb dissolution followed by automated analysis), it was not possible to perform a thorough evaluation because of suspected equipment failure. The dissolution of calcined ash scrap samples in commercially-fabricated bombs using the recommended medium (6 ml HNO_3 , 0.5 ml HF) resulted in numerous ruptures of the teflon liners and pressure relief discs. (Furthermore, only 52 to 82% of the uranium was dissolved even when the test did not fail, and the liners rapidly became distorted and unuseable). LASL reported similar failures with this apparatus in contrast to the high reliability previously obtained from bomb liners fabricated at their site. Investigations are underway at LASL to determine the cause of this discrepancy. (One likely factor under consideration is the variability in density or composition of the teflon material used as liners.) At present, work at NBL is directed to two approaches. In the first method a more dilute 8M HNO_3 acid mixture is used to control the reaction rate during dissolution. The second technique entails a sample pretreatment consisting of

TABLE I
RESULTS OF 12-DAY EVALUATION PROGRAM

Day	Based on Initial Calibration	Based on Daily Calibration	Average RSD, % ²
	Relative Difference, % ¹	Relative Difference, % ¹	
1	-0.26	-0.12	0.23
2	0.07	0.08	0.15
3	0.20	-0.06	0.18
4	-0.09	-0.02	0.18
5	-0.37	0.03	0.16
6	0.60	-0.02	0.14
7	0.21	0.02	0.12
8	0.19	-0.13	0.20
9	0.13	-0.23	0.24
10	0.28	0.08	0.21
11	0.10	-0.04	0.15
12	0.52	-0.06	0.21
Mean	0.13	-0.04	0.18
Range	0.97	0.31	0.12

1. Relative difference of the determined uranium values from the prepared value of the standards; average of four determinations at each of the nominal 4-,5-,6-,8-,10- and 12-mg U levels per day.
2. The average RSD of the determined g U/g values is the arithmetic mean of the RSD's for each level (4,5,6,8,10,12) on a given day.

TABLE II

RELATIVE STANDARD DEVIATION OF DETERMINED GRAMS URANIUM PER GRAM VALUES

U, mg <u>Level</u>	<u>DAYS</u>												<u>Average</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	
1	0.61	0.99	1.34	1.51	0.23	0.19	0.90	0.69	2.25	0.16	1.00	0.20	0.84
2	0.42	0.52	0.31	0.56	0.22	0.37	0.32	0.87	0.73	0.24	0.22	0.20	0.42
4	0.51	0.22	0.22	0.09	0.16	0.09	0.20	0.32	0.25	0.40	0.26	0.13	0.24
5	0.23	0.14	0.14	0.34	0.23	0.11	0.08	0.07	0.34	0.26	0.18	0.24	0.20
6	0.12	0.12	0.21	0.27	0.16	0.05	0.12	0.15	0.05	0.24	0.15	0.12	0.15
7	0.12	0.11	0.24	0.09	0.18	0.17	0.12	0.14	0.34	0.06	0.11	0.09	0.15
9	0.18	0.13	0.13	0.09	0.13	0.22	0.11	0.24	0.27	0.17	0.10	0.21	0.16
12	0.22	0.19	0.13	0.23	0.07	0.21	0.11	0.29	0.22	0.13	0.08	0.49	0.20
1-12 mg Average	0.30	0.30	0.34	0.40	0.17	0.18	0.24	0.35	0.56	0.21	0.26	0.21	0.30
2-12 mg Average	0.26	0.20	0.20	0.24	0.16	0.17	0.15	0.30	0.31	0.21	0.16	0.21	0.22
4-12 mg Average	0.23	0.15	0.18	0.18	0.16	0.14	0.12	0.20	0.24	0.21	0.15	0.21	0.18

TABLE III

THE EFFECT OF TEMPERATURE ON INSTRUMENT STABILITY

Day	Relative Difference, % ¹			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Temperature	22°C	30°C	23°C	18°C
4-mg U	-0.99	-3.32	-1.26	-0.05
6-mg U	-1.17	-2.82	-1.17	0.18
7-mg U	-0.86	-2.60	-0.92	0.00
10-mg U	-0.46	-2.55	-0.93	0.41
Average	-0.87	-2.82	-1.07	0.14
RSD, %	0.26	0.30	0.15	0.18

1. Relative difference of the determined uranium values from the prepared value of the standards; average of four determinations per standard.

the addition of 6 ml HNO_3 /0.5 ml HF, drying on a hotplate, addition of 6 ml 8M HNO_3 /0.5 ml HF, followed by bomb dissolution according to the recommended procedure. The former technique was not satisfactory but the pretreatment appears to be more effective. However, preliminary results are low indicating a possible loss of sample during pretreatment. The results obtained to date are given in Table IV. Additional development work on the bomb apparatus and technique is recommended prior to further evaluation studies.

A general appraisal of the system indicates that: (1) the AES can be used satisfactorily for the accurate analysis of uranium solutions at levels ranging from 1 to 12 mg with a precision varying from 0.3 to 1%; and (2) the bomb sample dissolution technique, although currently affected by construction materials problems, appears to be capable of acceptable performance after some additional study.

ACKNOWLEDGMENT

The authors wish to express their gratitude to Jere T. Bracey and Elaine Jacob for the statistical treatment of the data presented in this report and for their helpful suggestions in the evaluation; and to Glenn R. Waterbury, James E. Rein, Darryl Jackson and other Los Alamos Scientific Laboratory staff members for their cooperation and assistance in this program.

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2. Jackson, D. D., Hodgkins, D. J., Hollen, R. M. and Rein, J. E., "Automated Spectrophotometer for the Determination of Plutonium and Uranium", LA-6091, to be published.
3. Jackson, D. D., Hollen, R. M. and Rein, J. E., CMB-2047, (April 4, 1974), p. 4.

TABLE IV

COMPARISON OF RESULTS FOR CALCINED ASH SCRAP SAMPLES

Sample No	Dissolution Medium	% Uranium Dissolved	Automated Extraction Spectrophotometer g U/g ¹	NBL Titrimetric, g U/g ²
1	6 ml HNO ₃ , 0.5 ml HF	64.58	0.1315	0.1098
2	" "	77.54	0.0366	0.0331
3	" "	52.40	0.0028	0.0028
4	" "	68.06	0.0070	0.0067
5	" "	81.92	0.0076	0.0088
6	" "	65.89	0.0116	0.0100
7	" "	69.30	0.0068	0.0067
8	" "	77.32	0.0102	0.0092
9	6 ml 8M HNO ₃ , 0.5 ml HF	70.84	0.0086	0.0083
10	" "	81.93	0.0235	0.0260
11	" "	68.84	0.0279	0.0282
12	" "	74.02	0.0576	0.0587
13	" "	95.14	0.0061	0.0066
14	" "	93.52	0.0145	0.0166
15	" "	94.61	0.0154	0.0155
16	6 ml HNO ₃ , 0.5 ml HF	83.70	0.0305	0.0222
17	Pre-treatment	97.98	0.0382	0.0431
18	"	98.48	0.0392	0.0396
19	"	97.82	0.0368	0.0383
20	"	98.98	0.0373	0.0439
21	"	99.02	0.0427	0.0448

1. Samples dissolved by bomb dissolution technique; average of 2 determinations.
2. Samples dissolved by usual Na₂CO₃/NaNO₃ fusion technique; average of 2 or 3 determinations.

A LABORATORY QUALITY ASSURANCE PROGRAM FOR URANIUM ASSAY

C. E. Pietri, E. Jacob and J. T. Bracey

A quality assurance program is used at the New Brunswick Laboratory (NBL) to assure the reliability of the analytical data obtained from the determination of uranium in solution using the NBL titrimetric method. A revised improved program based on several years of experience has been formulated. Details of this program have been published.¹

REFERENCE

1. Pietri, C. E., Jacob, E. and Bracey, J. T., "A Laboratory Quality Assurance Program for Uranium Assay, NBL-276 (June 1975).

PREPARATION OF STANDARD "UNKNOWN" SAMPLES
FOR MEASUREMENT CONTROL

C. G. Goldbeck

In a report by Pietri,¹ et al, on the NBL quality assurance program for uranium assay, the general procedure followed for supplying "blind" or "unknown" standard samples to the analysts was outlined.¹ Reported here is a detailed method for the preparation of these standards. Included in the description are the preparation of the uranium master solution as well as the individual samples.

EXPERIMENTAL

Reagents and Apparatus

Hydrofluoric Acid.

Nitric Acid Solution, 8N.

Uranium Metal or Oxide, 99.9%⁺ (assay traceable to NBS SRM 960 or SRM 950a).

Glass Bottles, 500-ml volume and equipped with polycone seal caps.

Glass Flask, 5-liter volume.

Polyethylene Dispensing Bottles, 60-ml and 250-ml volumes.

Titration Beakers, sizes specified by analysts.

Procedure

A. Preparation and Storage of Master Solution

1a. Uranium Metal. Clean about 65 g of metal in 8N HNO₃ containing a few drops of HF. Rinse thoroughly with distilled water then with acetone. Dry with a lint-free towel and weigh to the nearest 0.01 mg. Calculate the actual weight of the metal by applying the proper buoyancy and purity corrections (Note 1).

1b. Uranium Oxide. Weigh out 77 g of oxide to the nearest 0.01 mg. Calculate the actual weight of oxide by applying the proper purity correction (Note 2).

2. Transfer the metal/oxide carefully to a preweighed 5-liter glass flask. Add 150 ml of 8N HNO₃ and warm the flask over low heat. Replenish the acid as needed until dissolution is completed and record the total amount of acid added.

3. Cool the solution to ambient temperature and bring to a total volume of 4 liters (acid and water) by adding distilled water in 300 to 500-ml portions and swirling after each addition. Reweigh the flask and calculate milligrams uranium per gram solution (Note 3).

4. Transfer the solution into 500-ml glass bottles (about 350 ml per bottle). Wipe the mouth of each bottle before tightening the cap then seal with plastic tape. Weigh each bottle to the nearest 0.1 g before storing it. Check this weight whenever a bottle is opened for the first time. Do not use it if a discrepancy greater than ± 0.1 g is observed (Note 4).

B. Preparation of "Blind" Standards

1. Transfer about 140 g of master solution to a 250-ml polyethylene dispensing bottle (or 60 g in a 60-ml bottle). Weigh the bottle to the nearest 0.01 mg then dispense an aliquant directly into a titration beaker. Mark the beaker with appropriate identification, reweigh the bottle and record the weight. Transfer another aliquant to another beaker, mark the beaker and record the bottle weight. Continue this process until the dispensing bottle is empty. Rinse the walls of each beaker with distilled water and cover with a watch glass.

2. Prepare about one month's supply of standards at a time or 30-40 samples per analyst. Provide a range which typifies sample sizes handled routinely in the laboratory. Suggested are:

Low Level Standard - 8 to 15 mg U

Medium Level Standard - 15 to 50 mg U

High Level Standard - 50 to 150 mg U

NOTE 1. The uranium metal air buoyancy correction for balance weights with an assumed density of 7.76 g/cm^3 is -0.0778 mg/g .

NOTE 2. No uranium oxide air buoyancy correction is necessary for balance weights with an assumed density of 7.76 g/cm^3 .

NOTE 3. The final uranium concentration is about 15 mg U/g solution.

NOTE 4. Data accumulated on two master solutions have shown that, with proper care in handling, these solutions can be stored for periods in excess of one year.

REFERENCE

1. Pietri, C. E., Jacob, E and Bracey, J. T., "A Laboratory Quality Assurance Program for Uranium Assay," NBL-276, (June 1975).

INTERLABORATORY EVALUATION ON MEASUREMENTS OF URANIUM HEXAFLUORIDE

C. D. Bingham and J. T. Bracey

A GAE Program on measurements of uranium hexafluoride was completed and the results released as a topical report.¹ Twenty-two laboratories in the USA and Europe measured the chemical purity (% UF_6) and the enrichment (% ^{235}U) of three samples monthly over a twelve-month period. Participants were asked to report chemical purity based upon their usual methods for high-precision uranium analysis. Four different materials, each of purity greater than 99.9% UF_6 , were used. A majority of the participating laboratories reported values whose means fell within $\pm 0.1\%$ of the values assigned to the chemical purity. Measurement bias was usually attributed to an assumed U_3O_8 stoichiometry of the ignition product of a gravimetric method.

The enrichment of the materials ranged from near-normal to approximately 1.7% ^{235}U . Most laboratory results fell within $\pm 0.2\%$ (relative) of the assigned enrichment values. There were wide variations in reported between-day precisions. Only ten laboratories measured enrichment with sufficient precision to identify four different enrichments. Of these ten, four laboratories exhibited a bias with respect to the assigned value. An evaluation of the calibration and standardization of mass spectrometric measurements in these laboratories is being carried out.

REFERENCE

1. Bingham, C. D. and Bracey, J. T., "Interlaboratory Evaluation on Measurements of Uranium Hexafluoride," NBL-274 (1975).

STATUS OF PHASE II OF THE INTERLABORATORY COMPARISON
PROGRAM ON THE ANALYSIS OF HTGR FUEL

N. M. Trahey and C. D. Bingham

During this report period, samples prepared by New Brunswick Laboratory (NBL)¹ were distributed for destructive assay. The laboratories participating in the program analyzed a set of four samples/month for ten months. Each set consisted of two urania-thoria mixtures, one BISO bead sample and one TRISO bead sample. The measurement data were forwarded monthly to NBL for statistical treatment. At the completion of all analyses, the data and the entire program design were evaluated. The results and conclusions will be presented and discussed by the participants at an information meeting in La Jolla, California in November 1975. Publication of all information generated through the program is scheduled for early 1976.

REFERENCE

1. Trahey, N. M. and Bingham, C. D., NBL-272 (October 1974).

COLORIMETRIC DETERMINATION OF IRON IN URANIUM OXIDE WITH FERROZINE

N. M. Trahey

Of the many reagents available for the colorimetric determination of iron, few are well-suited to trace analysis in uranium-bearing materials. Reagent choice is usually limited by interference effects of other impurities or uranium itself present in unseparated samples. Only ferroin-type compounds such as 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline have been consistently used for trace iron analyses without requiring extensive sample separations.

In this report are discussed the results obtained with ferrozine,¹ a triazine-type compound, which was used to determine iron in the NBL Standard Series No. 98 Uranium Oxide Spectrographic Samples. No separations were required in the analyses although the samples also contained 30 other impurity elements in varying concentrations.² By using the procedure written below, 2 μg Fe was easily measured in the presence of 200 mg uranium.

EXPERIMENTAL

Reagents

Acid Reagent Solution. Dissolve 1.3 g ferrozine and 25 g hydroxylamine hydrochloride in 25 ml distilled-deionized water. Add 125 ml HCl, cool, and dilute to 500 ml with distilled-deionized water.

Buffer Solution (pH = 5.5). Dissolve 100 g ammonium acetate in 300 ml distilled-deionized water. Add 88 ml NH_4OH and dilute to 500 ml with distilled-deionized water.

Iron Standard Solution (100 μg Fe/ml). Dissolve 0.05000 g electrolytic Fe (99.9%+ pure) in 25 ml HCl in a Pt dish. Transfer to a 500-ml volumetric flask and dilute to volume with distilled-deionized water. Make appropriate dilutions to prepare a calibration curve.

Uranium Standard Solution (100 mg U/ml). Dissolve 11.7930 g high purity U_3O_8 (< 4 μg Fe/g U) in 25 ml HNO_3 in a Pt dish. Transfer to a 100-ml volumetric flask and dilute to volume with distilled-deionized water.

Procedure

Weigh the uranium sample (0.1-1.0 g) into a Pt dish. Add 5 ml HNO_3 and, if necessary, 1 drop HF. Warm to dissolve then fume to incipient dryness and redissolve in 5 ml distilled-deionized water. Transfer entire sample or an aliquot containing ≤ 200 mg U to a 25-ml volumetric flask. Add 2 ml Acid Reagent Solution and boil for 10 min. Cool, add 2 ml Buffer Solution then dilute to volume with distilled-deionized water. Mix and let stand 1 min for complete color development. Measure at 562 nm in 1-cm cells using distilled-deionized water as reference. Prepare a calibration curve by carrying 0 to 50 μg Fe through the above procedure in the presence of 100 mg U.

RESULTS AND DISCUSSION

The effect of the yellow uranyl ion on the sensitivity of the magenta-colored Fe-ferrozine complex was investigated by comparing calibration curves prepared with and without uranium. As shown in Table I, 100 mg uranium had no effect and up to 300 mg uranium could be tolerated. In addition, reasonable reagent stability was verified when the data in Table I were reproduced with the same prepared reagents two months after the initial analyses were made.

TABLE I
COMPARISON OF IRON CALIBRATION CURVES
WITH AND WITHOUT URANIUM

<u>Fe, mg</u>	<u>U, mg</u>	<u>Optical Density</u>
0	0	0.011
0	100	0.013
0	300	0.015
1	0	0.020
1	100	0.019
5	0	0.060
5	100	0.060
10	0	0.106
10	100	0.106
10	300	0.115
20	0	0.200
20	100	0.203
40	0	0.409
40	100	0.409
50	0	0.497
50	100	0.498
50	300	0.501

Preliminary studies of impurity effects on the sensitivity were made by analyzing NBL Series No. 95 samples - levels 1 and 7 - whose Fe content have been certified by emission spectrographic and 1,10-phenanthroline colorimetric analyses. Since the same U_3O_8 matrix material was used to prepare No. 95 and No. 98 and the impurity concentrations were similar for both, analogous results could be expected. When no interference problems were encountered and the Fe content obtained agreed with the certificate value, the No. 98 samples were analyzed. Eight separate samples from each level were carried through the procedure and the results are shown in Table II. Sample sizes taken for 98-1 through 98-5 were 100 mg U each; for 98-6 and 98-7, 200 mg U samples were taken.

TABLE II
IRON ANALYSIS OF NBL STANDARD SERIES NO. 98

NBL Sample No.	Number Determinations	Average $\mu\text{g Fe/g U}$	RSD, %
98-1	8	515	0.5
98-2	8	215	1.8
98-3	8	113	2.6
98-4	8	58	2.2
98-5	8	32	1.7
98-6	8	20	3.7
98-7	8	13	6.4

This experiment did not attempt to explore the lower limit of detection for this method, however, the high extinction coefficient (27,900) of the Fe-ferrozine complex indicates that the method could easily be adapted to measure $0.1 \mu\text{g Fe/g U}$ - especially in separated samples.

REFERENCES

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2. New Brunswick Laboratory Provisional Certificate of Analysis, Standard Series No. 98(1-7) U_3O_8 Samples for Spectrographic Analysis.

TIME RESOLVED STUDIES FOR THE EVOLUTION OF ELEMENTS
BY CARRIER DISTILLATION FROM URANIUM OXIDE

H. G. Yuster

A time study method of element evolution from uranium oxide by carrier distillation is described. Time-spaced photography of accumulated counts generated from photomultiplier tube signals of the impurities present in the matrix is used for graphical presentation of data. Similar treatment of data from high purity uranium oxide permits corrections for background and dark current contributions to the various elements. Graphical differentiation of time increments versus increments of count rates results in a curve showing rates of element evolution as a function of time. Total time for complete evolution for each of the elements, an important factor in setting instrumental parameters, is clearly shown.

(To be submitted to the Journal of Applied Spectroscopy for publication.)

THE DETERMINATION OF MAGNESIUM IN BERYLLIUM
BY ATOMIC ABSORPTION SPECTROMETRY

R. L. GRAFF AND H. G. YUSTER

A procedure was developed for the determination of magnesium in beryllium by atomic absorption spectrophotometry which eliminates the hazards associated with the aspiration of beryllium into the burner of the instrument. In addition, the preparation of standards was simplified by the elimination of the need for magnesium free matrix material.

The proposed method is a modification of an unpublished New Brunswick Laboratory (NBL) procedure¹ for the determination of beryllium in magnesium in which beryllium is separated from magnesium by precipitation with ammonium hydroxide. The technique used here reverses the procedure by analyzing for magnesium in the filtrate. Briefly the method consists of dissolution with hydrochloric acid, precipitation of beryllium hydroxide with ammonia water, filtration and washing, and the analysis of magnesium in the filtrate with the use of prepared standards.

EXPERIMENTAL

Reagents and Apparatus

Magnesium Nitrate Standard Solution of 1000 μg Mg/ml.

Hydrochloric Acid - redistilled in quartz (approximately 20% HCl).

Ammonium Hydroxide - prepared from NH_3 and deionized distilled water. Saturated at 20°C (approximately 30% NH_3).

NBL Powdered Beryllium Metal Samples - having a range of approximately 100-400 $\mu\text{g/g}$ of Mg.

Atomic Absorption Spectrometer - Perkin-Elmer 403 with magnesium hollow cathode lamp.

Sample Preparation

Weigh 100 mg of the powdered beryllium sample into a 125-ml platinum dish. Add 10 ml of distilled deionized water and place the dish in an ice bath. Slowly add the hydrochloric acid until the metal is dissolved (note the volume of the acid). Stir, with a platinum rod and add ammonium hydroxide slowly to precipitate the beryllium hydroxide. When the solution is basic as shown by an indicator add 10% excess ammonium hydroxide (note the total volume

of ammonium hydroxide used). Filter the contents of the dish and wash at least three times with the dilute NH_4OH (note the volume needed for washing). Dissolve the precipitate in hydrochloric acid and repeat the precipitation. Combine the filtrates and the washings and adjust to 100 ml with water in a volumetric flask.

Preparation of Standards

Prepare individual calibration standards from a matrix containing quantities of HCl , ammonium hydroxide, and wash solution equivalent to those used in sample preparation. Add appropriate amounts of magnesium from the master solution to make a minimum of five standards. Include the matrix solution as a blank. Prepare the set of standards to cover an equivalent range of 1-100 $\mu\text{g Mg/ml}$ of solution.

Procedure

Follow the procedure outlined in the manufacturer's manual² for the determination of magnesium. Set the instrument to read in the 100-average mode. Measure the absorbance of the blank, the standards, and the sample solutions.

Plot absorbance of the standards versus concentration of magnesium. Determine the magnesium concentration in the samples from the calibration curve.

RESULTS AND DISCUSSION

In order to determine whether the procedure prescribed resulted in quantitative separation of the Mg , the $\text{Be}(\text{OH})_2$ residues were converted to the oxide and analyzed by an emission spectrograph technique which uses 5% Ga_2O_3 as a carrier material. The magnesium content of the residues ranged from 3-8% of the original concentration for the four samples with a single precipitation. This indicated good recovery for a single precipitation. Dissolution of the precipitate and re-precipitation reduces the magnesium content of the final $\text{Be}(\text{OH})_2$ to negligible levels thereby indicating complete recovery of the Mg .

Results of three different preparations on the four samples are summarized in Table I. Visual examination shows good precision for triplicate sampling.

TABLE I
MAGNESIUM RESULTS OF NBL BERYLLIUM SAMPLES

<u>Sample Preparation</u>	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>
1	220	140	390	120
2	200	140	390	110
3	220	170	390	120

REFERENCES

1. Zibulsky, H. private communication, New Brunswick Laboratory.
2. Perkin-Elmer, Analytical Methods of Atomic Absorption Spectrometry (1973).

AN INVESTIGATION OF THE LONG-TERM RELIABILITY AND
REPRODUCIBILITY OF A CONTROLLED-POTENTIAL COULOMETRIC
METHOD PROPOSED FOR THE DETERMINATION OF PLUTONIUM

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A procedure for the determination of plutonium by controlled potential coulometry using a gold working electrode in a nitric acid medium has been under evaluation at the New Brunswick Laboratory (NBL) for several years.¹ The initial work performed with plutonium indicated that the basic method was satisfactory. Subsequently, the method has been investigated further using iron as a substitute for plutonium.

This report describes experiments with iron which were performed primarily to assess the long-term reliability and reproducibility of coulometric measurements and includes procedures for instrument calibration and electrode conditioning.

EXPERIMENTAL

Reagents and Materials

Standard Iron Solution, 0.5 mg Fe/g solution, in 1N HNO₃, prepared from G. F. Smith No. 226 standard reagent grade iron metal (A) or Spex Industries iron rod (Lot No. 10741) (B). Assay was confirmed at 99.92 ± 0.04% (A) and 99.91 ± 0.05% (B), respectively.

Electrolyte, 1N HNO₃.

Sulfamic Acid, saturated solution.

Argon, purge gas, 99.996%.

Apparatus

Coulometer, M-T Electronics, Model 3.²

Reference Electrode, saturated calomel.

Counter Electrode, 0.05-cm diameter platinum wire in the shape of a helix.

Working Electrode, 1.59 cm x 38 cm, expanded gold sheet, coiled in four layers around a frame of 16-gauge gold wire (Figures 1 and 2). Prior to fabrication the expanded gold sheet is annealed at 900°C for 1 hour and allowed to cool to room temperature in the furnace.

Spiral Made of Expanded Gold Foil (1.59 cm x 38 cm)

FIGURE 1. GOLD WORKING ELECTRODE (TOP VIEW)

FIGURE 2. CELL HEAD

Digital Voltmeter (DVM), 10 V range, sensitivity 0.0001 V.

Cells, fabricated from 50-ml beakers, 3.73 cm i.d. minimum, 4.29 cm o.d. maximum, cut off at the top to provide a vessel 3.96 ± 0.08 cm tall. Cells are sealed with a teflon cap and Viton O-ring.¹ The complete assembly is shown in Figure 2.

Salt Bridges, teflon tubes with Vycor frits.

Stirrers, L-shaped wire sealed in polyethylene tubing and driven by a 6-V DC motor (~1200 rpm) controlled by a potentiometer.

Electrical Calibration Unit, consisting of a quartz crystal clock (capacity 999.99 sec, accurate to ± 0.01 sec), a 1000-ohm precision resistor, and an appropriate switching mechanism.

Procedure

Calibration

Adjust and set the coulometer controls as described in the coulometer manufacturer's instruction manual² using the 27-ohm load resistor specifications. Set the readout voltage divider at 0.5000. Turn the calibration unit power switch ON. With the calibration unit on STOP and the potentiostat on STANDBY, connect the calibration unit to the potentiostat. Connect the DVM to the calibration unit. Turn the potentiostat to OPERATE and the calibration unit to START. Record the potential drop across the resistor as displayed by the DVM. This is indicative of the current flowing through the calibration unit. Turn the calibration unit to STOP and the potentiostat to STANDBY. Disconnect the DVM from the calibration unit and reconnect the DVM to the integrator. Reset the timer, turn the potentiostat to OPERATE, and the calibration unit to START. Allow the calibration unit to run for about 10 minutes and turn the unit to STOP. Record the DVM readout and the exact calibration time. Turn the potentiostat to STANDBY, turn the calibration unit power switch OFF, and disconnect the calibration unit. Reattach the cell leads to the potentiostat.

Calculate the electrical calibration factor, C, according to equation (1), as follows:

$$C = \frac{PDt}{RV} \quad (1)$$

where:

C = electrical calibration factor,
coulombs/volt

P = potential drop across precision
resistor, volts

D = integrator divider setting

t = calibration time, seconds

R = value of precision resistor, ohms

V = integrator DVM reading, volts

Calibrate the coulometer at the beginning of each day. The electrical calibration factor should be within $\pm 0.03\%$ of the cumulative mean value previously established for the particular coulometer. If not, make two additional calibrations. If both of these runs are not within 0.03% of the mean, perform a drift test as described. If the drift is within limits, then submit the instrument for servicing.

Drift Test

Perform a drift test if a reading on the DVM changes while the potentiostat is set on HOLD or if the calibration factors are not within limits.

To perform a drift test, allow the coulometer to stabilize in STANDBY position for at least 30 min, or make the test prior to calibration of the instrument. Disconnect the leads to the electrodes and short the counter electrode terminal to the reference electrode terminal. Turn the potentiostat to OPERATE for a known period of time, usually 15 min. Calculate the drift rate and make any adjustments according to the instruction manual.² Deviations from this procedure may introduce significant errors in the drift test due to capacitor hysteresis.

Sample Analysis

Rinse the cell head and components thoroughly with $1N\ HNO_3$. Refill the salt bridges with $1N\ HNO_3$. Insert the platinum counter electrode and the saturated calomel reference electrode (SCE) into their proper salt bridges. Determine a blank correction as follows: Add to the cell 5 drops of sulfamic acid solution and 18 ml of $1N\ HNO_3$ making sure that the gold electrode is covered. Assemble the cell to avoid air leaks and adjust the argon purge gas tube so that the inlet end is ~ 3 mm above the liquid surface. Set the gas flow rate to give a "dimple" of about 2 mm deep in the liquid surface, start the stirrer, and adjust its speed to give rapid stirring (~ 1200 rpm) without splashing. Reduce at $0.3000 + 0.0001\ V\ vs.\ SCE$ to $< 10\ \mu A$ background current (usually 1 to 2 min). Oxidize at $0.7000 + 0.0001\ V\ vs.\ SCE$ to $< 10\ \mu A$ background current (approximately 4 to 5 min). Record the elapsed oxidation time to 0.1 min, the readout voltage, and the current. After 3 min again accurately record these values.

If the oxidation and reduction background currents noted are not obtained, clean the cell, replace the electrolyte and repeat the blank determination. If a satisfactory response is not obtained clean the electrode/cell head according to the recommended procedures.

Stop the stirrer, turn potentiostat to STANDBY, remove the cell from the head, and transfer the electrolyte (blank) to a second cell containing the iron standard (2 mg Fe) making sure to wash the cell walls. Reassemble the cell and head, and adjust the gas flow and stirrer.

Analyze the sample as follows: Reduce and oxidize the sample and record the necessary data following the blank procedure above. Reduction times should range from 8 to 15 min, oxidation times from 7 to 15 min. At the conclusion of the sample oxidation, set the

coulometer potentiostat to STANDBY, stop the stirring, remove the cell and discard the sample. Rinse the cell and cell head thoroughly with 1N HNO₃ only. Continue with the next sample by repeating the blank and sample procedures above.

If no further analyses are to be made shut down the system as follows: Turn off the purge gas, remove and store the SCE, replace the acid in salt bridge tubes rinsing twice with 1N HNO₃ and insert a cell filled with 8N HNO₃ under the cell head assembly. Set the potentiostat to STANDBY when not in use.

Calculation of Results

Calculate the mass of material determined using equation (2), as follows:

$$W = \frac{C M 10^3}{F D n N_C} \left[\left(\frac{E_3 t_4 - E_4 t_3}{t_4 - t_3} \right) + \left(\frac{E_2 t_1 - E_1 t_2}{t_2 - t_1} \right) \right] \quad (2)$$

where:

W = mass of element determined, mg

C = electrical calibration factor, coulombs/volt,
from equation (1)

M = atomic mass of element determined, g/mole

F = Faraday constant, coulombs/equivalent

D = integrator readout voltage divider setting

n = electron change in electrochemical reaction,
equivalents/mole

N_C = Nernst correction, calculated quantity
electrolyzed/total quantity present

E₁ and t₁ = integrator DVM readout, volts, at first
elapsed time, min, for blank

E₂ and t₂ = integrator DVM readout, volts, at second
elapsed time, min, for blank

E₃ and t₃ = integrator DVM readout, volts, at first
elapsed time, min, for sample

E₄ and t₄ = integrator DVM readout, volts, at second
elapsed time, min, for sample.

Calculate the per cent standard element recovery using equation (3), as follows:

$$\% \text{ Recovery} = \frac{W}{S} 100 \quad (3)$$

where:

W = mass of element determined, mg, from equation (2)

S = weight of element added, mg.

Cleaning Procedure

Clean the electrodes only when necessary, that is, when the electrolysis times become excessive, initial backgrounds of 20-30 μ a are encountered, or final backgrounds of ≤ 10 μ a are difficult to achieve. The HCl cleaning procedures described below are strenuous treatments and may eventually destroy the electrode if not used with care. Several methods have been used successfully and are noted below in order of preference.

Method 1

Remove the reference and counter electrodes from the cell head, empty the electrolyte from the salt bridges and rinse twice with water, remove the glass cell and discard the electrolyte. Insert a clean cell filled with distilled water under the head and stir for 1 min to insure removal of HNO_3 . Remove the cell and blot the bottom of the gold electrode with lintless absorbent paper to remove excess liquid. Heat 20 ml of concentrated HCl in a cell to 65°C , insert under the head so that the electrode coils and salt bridge frits are completely covered; do not allow the acid to come in contact with the O-ring seal. If acid does contact the O-ring, clean the head thoroughly and change the O-ring. Stir for 1 min, remove the cell, rinse the working electrode and cell head components thoroughly with water as described above to remove all HCl and blot the electrode as before. Rinse the salt bridges twice with 1N HNO_3 and refill with concentrated HNO_3 . Insert a cell filled with concentrated HNO_3 under the cell head and allow the working electrode to stabilize for approximately 8 hr. Clean the counter electrode with warm HCl as above rinse with water, insert in its salt bridge, and allow to stabilize as above.

Method 2

If the previous cleaning technique does not provide a satisfactory electrode response, repeat Method 1 above with the following modification. After the initial rinsing of electrode and cell head with water, fill the salt bridges with acetone, insert a cell filled with acetone under the cell head and allow to stand for 1 hr with occasional stirring. Rinse the cell head and components thoroughly with water as before and proceed with the HCl treatment described in Method 1. Clean the counter electrode as in Method 1 using HNO_3 -HCl (1:1).

Method 3

If the previous two methods are not satisfactory, remove the gold electrode from the cell head and place in a cell filled with 14N HNO₃. Heat the solution and maintain at about 90°C for about 30 min. Rinse the electrode with water and allow it to stabilize in cold concentrated HNO₃ for at least four hr.

RESULTS AND DISCUSSION

The current procedure for the controlled-potential coulometric determination of iron, as a substitute for plutonium, was evaluated over a period of nine months by three analysts. The results are summarized in Table I and indicate satisfactory precision and accuracy.

TABLE I

ACCURACY AND PRECISION OF CONTROLLED-POTENTIAL COULOMETRY

<u>Analyst</u>	<u>Standard</u>	<u>Number of Determinations</u>	<u>Average Recovery, %</u>	<u>RSD, %</u>
1	A	185	100.01	0.03
2	A	45	100.02	0.03
3	A	56	99.98	0.05
1	B	15	99.99	0.02
2	B	17	99.96	0.02

Electrical calibration of the coulometer is adequate for use in the analysis of samples. The calibration value for three coulometers during the 9-month study period varied less than 0.023% (RSD) for 216 calibrations.

Under optimum operating conditions, a coulometric determination (including the blank determination) can be completed in 22 to 35 min, depending on the condition of the electrode. Average running times for standards are about 28 min, permitting as many as twelve determinations per day to be performed under actual operating conditions. Although running times as long as 35 min have been experienced even under optimum conditions at the end of a day, storage of the gold electrode in 8N nitric acid overnight has restored most of its sensitivity the following day. Typical data are presented in Table II. Again, under optimum operating conditions, an electrode performs satisfactorily (acceptable precision, accuracy, and speed) generally for at least 30-40 determinations or 3-4 days before a cleaning treatment is required.

TABLE II
CONDITIONING OF GOLD ELECTRODES IN 8N HNO₃

<u>Day</u>	<u>Running Time, min</u>		
	<u>Initial</u>	<u>Final</u>	<u>Average</u>
1	22	31	28
2	24	35	28
3	25	31	29

The proposed procedure, when applied to plutonium analysis and verified by NBS standard plutonium materials, is expected to give results comparable to the data obtained for iron in this present study.

ACKNOWLEDGMENT

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PRELIMINARY EVALUATION OF AN AUTOMATED COULOMETRY SYSTEM (AUTOCOULOMETRY) FOR PLUTONIUM

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An autocoulometry system is part of an overall plan for the automation of the coulometric determination of plutonium^{1,2} at the New Brunswick Laboratory (NBL). Progress in the design, construction and testing of individual components has been described previously.^{3,4} This report describes the testing and mechanical and electrical performance of the entire system in routine operation (both single and dual coulometer head modes) using iron as a substitute for plutonium.

Reagents and Apparatus

The system consists of a 13-module apparatus in which a sample handler automatically delivers cells containing solutions to dual coulometer cell heads for analysis. Each cell head is connected to a separate coulometer. A description of the modules has been reported.⁴

Standard Iron Solution, 0.5 mg Fe/g in 1N HNO₃, prepared from G. F. Smith No. 226 standard reagent grade iron as previously described.²

Stirrer, similar to the type described² and run at a constant speed of 900 rpm.

Other reagents and apparatus previously have been described.²⁻⁴

Procedure

Calibration

Calibrate the coulometers as previously described prior to each series of runs.²

Sample Analysis

Accurately weigh aliquots of the iron standard solution into coulometer cells to give approximately 2 mg Fe per sample and evaporate to incipient dryness. Load five cells into each cell transfer tray and place in position on the sample handler. Prepare the cell head and components for operation as previously described.² Turn on the master power and the printer switches. (The coulometers and DVM's should always be on; the auto-manual control switch is in the HOLD position.) Flip the auto-manual control switch from the HOLD (manual) to the RUN (auto) position on the control module.

The following automatic sequences (controlled by the preset times tabulated below) occur: The 8N HNO_3 solution in which the electrodes are stored is aspirated to waste; the cell and electrodes are cleaned twice with fresh 1N HNO_3 electrolyte which is aspirated to waste. (These sequences comprise steps 12 through 16 of the programmed cycle and prepare the system for continuous services.) The electrolyte (blank) is added to the clean cell (step 17). The blank is reduced at 0.3000 V; the potential is switched; the blank is oxidized at 0.7000 V; two digital voltmeter (DVM) readings (taken 3 min apart) are printed out; the blank solution is aspirated to the storage reservoir; the cell containing the sample is advanced under the cell head and the blank solution is transferred into this cell. (These sequences comprise steps 1 through 7 of the programmed cycle and determine the blank value for the sample to be analyzed.) The sample is reduced/oxidized and the results are printed out in the same manner as for the blank. (These sequences comprise steps 8 through 11.)

At this point (step 12) the cycle is repeated for the next sample. At the termination of all sample analyses flip the auto-manual control switch from RUN to HOLD; turn off the printer and master power switches. Rinse the cell, cell head, and working electrode thoroughly with 1N HNO_3 . Follow the shutdown procedure for manual coulometry.² Sequences and preset times for automatic operation are shown in Table I.

TABLE I
SEQUENCES AND PRESET TIMES

Step	Operation	Preset Time, min	
		Single Head Mode (Preliminary)	Dual Head Mode
1	Blank reduction*	8.0	6.0
2	Potential switching	-	-
3	Blank oxidation*	10.25	8.75
4	Printout	-	-
5	Blank storage	2.0	2.0
6	Sample advance	-	-
7	Blank release	2.25	2.25
8	Sample reduction*	40.0	28.0
9	Potential switching	-	-
10	Sample oxidation*	24.5	22.5
11	Printout	-	-
12-16	Cleaning	12.0	12.0
17	Electrolyte (blank) addition	1.0	1.0
18	Vacant	-	-
	Total	100.0	82.5

* Taken to 10 μa background current.

Electrode Cleaning. Cleaning is usually indicated when the electrode response is sluggish, i.e., initial backgrounds of 20-30 μ a, extended redox times, and difficulty in achieving final backgrounds of $\leq 10 \mu$ a. The following procedure is satisfactory for cleaning the autocoulometer head and electrodes. However, if this procedure does not restore the electrodes to proper operation, alternative procedures are available.² Raise the cell head and rinse thoroughly with distilled water to remove all HNO_3 . Warm 30 ml of concentrated HCl in a coulometer cell to about 65°C and place the cell in a stainless steel tray in the position directly under the head. Lower the head into the warm acid and allow to stand with stirring for 3-5 min. Raise the cell head and rinse thoroughly with distilled water to remove all acid. Lower the cell head into a coulometer cell containing 30 ml of concentrated HNO_3 and store for a minimum of 8 hr before use.²

Calculations

Calculate the per cent iron recovery from the digital voltmeter readout taken for both the blank and sample oxidation sequences according to the method previously described.²

RESULTS AND DISCUSSION

Separate studies were made to determine the correct Agastat programmer time settings for reagent delivery and storage of electrolyte, and removal of the analyzed solution. The maximum sequence time settings given in the procedure for the oxidation/reduction steps were established by electrolysis of a series of blanks and samples to a background current of 10 μ a. The correct stirrer position and speed to give optimum stirring without splashing were determined. These parameters were established prior to the start of sample runs.

The evaluation of the instrument consisted of two parts: single coulometer head operation, and simultaneous operation of both heads.

Single Head Operation

The overall running time for a complete cycle was 99 min. A summary of the individual times for each sequence is given in the procedure. Some reductions in the various sequence times were considered possible. However, the major interest was in determining the electromechanical reliability of the system and economies in operating time were considered as secondary. Nine evaluation runs were made, each one lasting from 27 to 33 hours of continuous operation. All runs operated automatically and unattended during these periods, except in Run No. 1 where laboratory personnel were in attendance to observe and record details of the total system performance. The results of these tests are given in Table II and indicate an average per cent recovery ranging from 99.88 to 100.06 with an average per cent relative standard deviation (RSD, %) ranging from 0.03-0.09%. Statistical evaluation of the data show that the initial runs (Nos. 1 and 2) were significantly different in respect to precision from the remaining seven runs. The per cent recovery and RSD, %, for runs Nos. 3-9 ranged

from 99.88 to 99.98% and from 0.03 to 0.08%, respectively. Evaluation of data from the analysis of the same standard material by manual coulometry gave values of 100.01% recovery with a precision of 0.03% RSD.² Recovery values are slightly lower for autocoulometry than for manual coulometry. Although the range of precision obtained for autocoulometry runs is wider than for manual coulometry there is no statistically significant difference in the precision of both methods.

TABLE II
SINGLE HEAD OPERATION

<u>Run No.</u>	<u>Number of Samples</u>	<u>Number of Failures</u>	<u>Average Recovery, %</u>	<u>RSD, %</u>
1	24	1	99.93	0.09
2	19	3	100.01	0.09
3	19	3	99.92	0.04
4	16	3	99.88	0.05
5	18	0	99.89	0.05
6	19	3	99.95	0.08
7	19	1	99.90	0.04
8	16	4	99.98	0.04
9	20	3	99.94	0.04
Total	170	21		

There were 21 samples (12%) out of a total of 170 samples which failed during these tests. The failures were caused by stirrer malfunction (62%), printer malfunction (10%), sample handler malfunction (4%), and unknown reasons (24%). The major malfunction was the electromechanical performance of the stirrer: sporadic inability to start. The potentiometer setting for the stirrer motor which provided satisfactory operating speed was inadequate to overcome the initial starting resistance of the system. This malfunction was corrected by redesign of the stirring mechanism to allow increased voltage input to the motor while maintaining stirring speeds in the correct operating range during analysis.

Dual Coulometer Head Operation

The second phase of the evaluation consisted of dual head operations in which preliminary short-term daily runs were made prior to final extended time tests. Experience gained in single head operation allowed the operating times to be reduced to 81.5 min per sample, as indicated in the procedure, and to 24 hours per run cycle. Four preliminary runs with both heads operational for 8-hour periods only, gave recoveries of 99.96% (0.03% RSD) and 99.97% (0.05% RSD). Limited data indicated no significant differences in results between heads or among runs. Subsequently, three attended evaluation runs were made which lasted approximately 24

hours each. The results of these tests are given in Table III and indicate average percent recoveries of 99.97% (0.03% RSD) for the left head and 100.00% (0.04% RSD) for the right head. Although the difference in percent recovery between heads was small it was statistically significant; there were no differences in respect to precision. These results compare favorably to manual coulometry data (100.01% recovery, 0.03% RSD) and to the prepared value of the standard material. Only nine sample failures (8%) out of 114 samples occurred. The causes of these failures were incomplete reduction of sample or blank (78%), stirrer malfunction (4%), and unavoidable accidents (10%). The major malfunction in this series of tests was caused by incomplete reduction of either blank or sample at the right head due to a sluggish electrode response. This malfunction, a normal occurrence in electrochemical processes, was corrected by cleaning and conditioning the electrode as described in the procedure.

The performance of the autocoulometry system, as tested with iron standards, appears to be satisfactory. The relative accuracy and precision of the dual coulometer cell head operation is acceptable: The goal of automated coulometric analysis with a precision of 0.1% RSD or less has been achieved with iron as a stand-in for plutonium. The instrument's overall operational reliability is satisfactory; however, several minor malfunctions need to be corrected. The next phase of the evaluation will consist of installation of the autocoulometry system in the gloved box and subsequent testing with plutonium.

TABLE III
DUAL HEAD OPERATION

<u>Run No.</u>	<u>Number of Samples</u>	<u>Left Head</u>		
		<u>Number of Failures</u>	<u>Average Recovery, %</u>	<u>RSD, %</u>
1	21	0	99.99	0.03
2	18	2	100.00	0.02
3	18	0	99.95	0.03
		<u>Right Head</u>		
1	21	4	100.00	0.02
2	18	3	99.96	0.06
3	18	0	100.01	0.03

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THE RESPONSE OF GOLD ELECTRODES FOR USE IN CONTROLLED-POTENTIAL COULOMETRY

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Gold working electrodes have been used satisfactorily on a limited basis at the New Brunswick Laboratory (NBL) for the controlled-potential coulometric determination of plutonium.¹ The design of the NBL automated coulometry system (autocoulometry) for plutonium²⁻⁴ permits the simultaneous operation of two coulometer cells with similar operating characteristics. Manual coulometry also requires consistent response among electrodes for satisfactory operation.⁵ The reliability of several gold electrodes, hand-crafted at NBL and thus varying somewhat in physical dimensions, was examined. This study was made to determine the precision of measurements made with several of these fabricated gold electrodes, to estimate the accuracy of these measurements, and, subsequently, to examine the suitability of these electrodes for autocoulometry and manual coulometry. Accordingly, three different operators analyzed at least fourteen standards with each of the three electrodes using the same equipment, in order to obtain sufficient data for evaluation. In this investigation iron was used as a substitute for plutonium.

EXPERIMENTAL

Reagents and Apparatus

Standard Iron Solution, 0.5 mg Fe/g solution (1N HNO₃) prepared as previously described.⁵

Gold Electrodes. Three working electrodes were fabricated by hand from expanded gold sheet coiled in layers around a gold wire support. A detailed description is given elsewhere.⁵

Other apparatus and reagents, previously described.^{1,5}

Procedure

Accurately prepare iron solutions to give about 2 mg Fe per sample, calibrate the coulometer, clean the electrode when necessary, determine the blank and sample by controlled-potential coulometry, and calculate the results in terms of per cent iron recovery, as described.⁵

RESULTS AND DISCUSSION

From 14 to 22 aliquots of the iron standard solution were run coulometrically by each of three analysts using three different gold electrodes and the same instrumentation. Although there are

some statistical differences for iron recovery and precision among the three electrodes and analysts, the data are acceptable, Tables I and II. The poorest precision obtained by any analyst for any electrode was 0.09% (relative standard deviation, RSD). The maximum difference between average iron recovery values was 0.08%; these values ranged from 99.94 to 100.02% of the known standard.

TABLE I
COULOMETRIC ANALYSIS USING GOLD ELECTRODES

<u>Analyst</u>	<u>Electrode No. 1</u>		<u>No. of Determinations</u>
	<u>Fe Recovery, %</u>	<u>RSD, %</u>	
A	99.91	0.074	19
B	99.96	0.033	14
C	99.94	0.078	14
<u>Electrode No. 2</u>			
A	100.00	0.036	15
B	100.04	0.022	15
C	100.01	0.022	15
<u>Electrode No. 3</u>			
A	99.96	0.087	22
B	100.04	0.040	17
C	99.99	0.014	15

Some of the small statistical differences calculated from the data in Table I may have been generated by slight variations in initial analyst operations. For example, there were some minor differences in the electrode cleaning and overnight storage techniques which became standardized among the analysts later on in this study. In some initial runs the electrodes were stored in 1N HNO₃ apparently resulting in poorer precision than in later determinations made after storage in 8N HNO₃. Similarly, the warm HCl electrode cleaning method⁵ gave good electrode response and precision for electrodes 1 and 2 but was unsatisfactory for electrode 3. An alternative method, the warm HCl/acetone/HCl treatment⁵ was later found to be effective.

TABLE II

DATA SUMMARY FOR GOLD ELECTRODE STUDY

<u>Electrode</u>	<u>Total No. of Determinations</u>	<u>Average Recovery, %</u>
1	47	99.94
2	44	100.02
3	54	100.00

Generally, the results obtained in this study indicate that gold electrodes are suitable for use in both manual coulometry and autocoulometry with a precision and relative error of less than 0.1%.

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THE EFFECT OF ION-EXCHANGE SEPARATION PROCEDURES ON CONTROLLED-POTENTIAL COULOMETRIC ANALYSIS

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Many plutonium samples received at the New Brunswick Laboratory (NBL) for analysis are not directly analyzable by controlled-potential coulometry¹ because of their high impurity and/or salt content. Frequently these samples contain organic matter which quickly poisons the electrode. Thus, after dissolution of samples, an ion-exchange separation of plutonium from impurities² is considered necessary for reliable results.

At present, plutonium solutions purified by ion-exchange separations are fumed three times with sulfuric acid to insure destruction of organic matter, eliminate halogens and provide a soluble material for coulometric analysis. This study was made to determine the effect of any residual matter resulting from this ion-exchange process and to determine the minimum number of fumings necessary for satisfactory coulometric analysis. The effect on coulometry of some of the reagents used in this process was studied, such as the HCl-HF eluting solution and the H₂SO₄ solution used for fuming.

In this preliminary work iron was substituted for plutonium.

EXPERIMENTAL

Reagents and Apparatus

Reagents and apparatus are described elsewhere.^{1,3}

Procedure

Preparation of Blank Solutions

Using the Autosep apparatus³ prepare a sufficient number of blank solutions for the preparation of sample solutions (Sets A, B and C) described below. To prepare these blanks, pass 30 ml of 0.36N HCl-0.01N HF eluting solution through Dowex 1-X2 resin columns prepared as described in a previous report.¹ Collect the eluates (blanks) in coulometric cells and evaporate to incipient dryness.

Preparation of Sample Solutions

Set A. To the first set of about 25 blanks, add 5 ml of 0.1N H₂SO₄ and one drop of concentrated sulfuric acid. Heat to fumes of SO₃ and continue heating until all fumes have disappeared

and then heat an additional ten min. Spike, by weight, each blank with an aliquant of the standard iron solution containing about 2 mg of iron and evaporate to incipient dryness.

Set B. Repeat the procedure for Set A and then fume the samples a second time.

Set C. Repeat the procedure for Set A and then fume the samples three times.

Set D. Add 30 ml of 0.36N HCl-0.01N HF eluting solution and 1 ml of 8N HNO₃ wash solution to each of 75 clean coulometer cells. Evaporate to dryness and fume twice with sulfuric acid as described above. Spike each cell, by weight, with the standard iron solution as above and evaporate to incipient dryness.

Set E. Add 5 ml of 0.1N H₂SO₄ and 1 drop of concentrated sulfuric acid to each of about 25 coulometer cells and fume twice as described above. Spike each with the standard iron solution as above and fume to incipient dryness.

Preparation of Standard Solutions

Set F. Add weighed aliquants of the standard iron solution into each of about 50 coulometer cells as above and evaporate to incipient dryness. Analyze all prepared samples and standards by controlled-potential coulometry.⁴

RESULTS AND DISCUSSION

The data from these experiments were examined statistically. Results for the analysis of samples treated by the ion-exchange process did not differ between sets A, B and C but were significantly different from the results obtained on untreated standards, Table I. Recovery values were appreciably higher and less precise for the treated samples than for standards. Although operating times were about average for both samples and standards, the working electrode required more frequent cleaning during the sample runs. Among sample sets A, B and C there were no differences in operating characteristics (electrode response time and cleaning frequency). Furthermore, a single sample fuming with sulfuric acid appeared to be as effective as multiple fumings.

Results for both the HCl-HF and H₂SO₄ treated samples as a group were marginally significantly different from results obtained on standards. The recovery values were slightly higher and less precise for the HCl-HF samples than for standards, Table II. Overall operating times for these samples were longer than average, varying from 29 to 36 min. The operating time near the conclusion of some runs reached 47 min; cleaning the electrode substantially reduced this time to 26 min. There was a slightly higher frequency of required electrode cleaning for these runs than for the analysis of standards. Recovery values were slightly higher for H₂SO₄ treated samples than for standards but as precise. No differences in operating characteristics were exhibited.

TABLE I

THE EFFECT OF ION-EXCHANGE PROCESSES ON COULOMETRY

<u>Set</u>	<u>Description</u>	<u>No. of Determinations</u>	<u>Recovery, %</u>	<u>RSD, %</u>
A	Ion exchange (1 fuming)	19	100.18	0.08
B	Ion exchange (2 fumings)	21	100.19	0.09
C	Ion exchange (3 fumings)	24	100.11	0.13
F	Standards	44	100.01	0.02

TABLE II

THE EFFECT OF REAGENTS ON COULOMETRY

<u>Set</u>	<u>Description</u>	<u>No. of Determinations</u>	<u>Recovery, %</u>	<u>RSD, %</u>
D	HCl-HF	63	100.05	0.06
E	H ₂ SO ₄	25	100.04	0.03
F	Standards	44	100.01	0.02

The substantial effect observed in data from the samples processed by ion-exchange separation is postulated to be caused by material leaching from the resin or ion-exchange columns. The contribution of the reagents to this effect appears to be marginal. The effect noted in the HCl-HF tests may be caused by impurities either leached from the glass cells or in the reagents. Additional studies with both iron and plutonium are planned to further investigate the effects of the ion-exchange separation on controlled-potential coulometry.

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APPENDIX

Standard Samples Available at NBL

Analyzed samples currently available from the New Brunswick Laboratory fall into four categories: 1) ore samples for checking chemical analyses, 2) ore samples mixed primarily for use as counting standards, 3) metals or compounds of typical production quality from the nuclear industry certified for impurities present and/or major component, 4) spectrographic standards consisting of oxides containing added impurities in graded series. Additional materials are in various stages of planning.

Powdered Ores

<u>Sample No.</u>	<u>Material</u>	<u>Sample Wt. g/bottle</u>	<u>Description</u>
1	Phosphate Rock	100	Natural rock containing 0.029% U_3O_8
3-B	Diluted Pitchblende	100	Pitchblende diluted with dunite giving U_3O_8 content of 3.9%
4	Carnotite	100	Natural ore from Colorado Plateau containing 0.18% U_3O_8
5	Carnotite	100	Natural ore from Colorado Plateau containing 0.11% U_3O_8
6-A	Pitchblende ore	50	Natural Congo ore containing 67.9% U_3O_8
7-A	Monazite sand	100	Natural ore containing 9.7% ThO_2 , 0.4% U_3O_8

Ore Counting Standards

42(1-4)	Diluted pitchblendes for calibrating counting equipment	100 each	Pitchblende diluted with dunite to give 4.0, 2.0, 1.0 and 0.5% U.
74-A	0.1% U pitchblende in dunite	100	74-76 Series consists of pitchblende diluted with dunite.
76-B	0.01% U pitchblende in dunite	100	

Ore Counting Standards

<u>Sample No.</u>	<u>Material</u>	<u>Sample Wt. g/bottle</u>	<u>Description</u>
79-A	1.0% Th, 0.04% U	100	79-82 Series consists of monazite sand diluted with dunite
80-A	0.1% Th, 0.004% U	100	
82-A	0.02% Th, 0.0008% U	100	
101	1% U	50	Series 101 through 105 consists of pitchblende ore diluted with ground silica sand
102	0.1% U	50	
103	0.05%U	50	
104	0.01% U	50	
105	0.001% U	50	
106	1% Th, 0.04%U	50	Series 106-110 consists of monazite sand diluted with ground silica sand
107	0.1% Th, 0.004% U	50	
108	0.05% Th, 0.002% U	50	
109	0.01% Th, 0.0004% U	50	
110	0.001% Th, 0.00004% U	50	

Metals and Compounds

17-B	UF ₄	200	Product material analyzed for U, U ⁺ ⁴ , UO ₂ (A.O.I.)
18	UO ₃	500 or 10-50	Product material analyzed for total U, H ₂ O, NO ₃ , HCl insoluble, and impurities
85	Be metal (powdered)	100	Be metals analyzed for impurities: B, N, C, Cu, Pb, Cd, Mo, Ni, Zn, Co, O,
86	" " "	100	
87	" " "	100	
88	" " "	100	
97	UO ₂ 2.38% enrichment	100	UO ₂ material of low enrichment for U assay and U isotopic assay

Spectrographic

<u>Sample No.</u>	<u>Material</u>	<u>Sample Wt. g/bottle</u>	<u>Description</u>
66(1-7)	ThO ₂	25	A graded series of 6 plus matrix for determination of Al, Bi, Be, B, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, K, Si, Ag, Na, Sn, V, Zn
96(1-6)	BeO	10	A graded series of 5 plus matrix for determination of Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sn, Sr, Ti, Zn
98(1-7)	U ₃ O ₈	25	A graded series of 6 plus matrix for determination of Ag, Al, Ba, Be, Bi, B, Ca, Cd, Co, Cr, Cu, Fe, In, K, Li, Pb, Mg, Mn, Mo, Ni, P, Si, Sb, Sr, Na, Sn, Ti, V, W, Zn.

¹ Dual Capacity