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ANNUAL PROGRESS REPORT FOR THE PERIOD JULY 1969–JUNE 1970

June 1971

New Brunswick Laboratory
U. S. Atomic Energy Commission
New Brunswick, New Jersey

UNITED STATES ATOMIC ENERGY COMMISSION · DIVISION OF TECHNICAL INFORMATION

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CHEMISTRY (TID-4500)

UNITED STATES ATOMIC ENERGY COMMISSION

ANNUAL PROGRESS REPORT FOR THE PERIOD JULY 1969 THROUGH JUNE 1970

AEC Research and Development Report

Carleton D. Bingham, Director

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June 1971

NEW BRUNSWICK LABORATORY

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ABSTRACTS

Application of the New Brunswick Laboratory (NBL) Titrimetric Method (Ferrous Ion Reduction) to the Precise Assay of Uranium Metal

The NBL titrimetric method (ferrous ion reduction) of determining uranium has been modified for the high precision assay of uranium metal. A precision of about 0.005% (coefficient of variation) can be obtained. The accuracy was assessed by the analysis of NBL dingot uranium metal.

Titrimetric Determination of Total Uranium and Uranium(IV) in Uranium Dioxide

The total uranium in uranium dioxide can be determined by a modified NBL titrimetric method (ferrous ion reduction) with high precision. The uranium(IV) apparently can also be determined by a further modification of the same method enabling the uranium(VI) to be calculated by difference.

Titrimetric Determination of Uranium at the 10- and 20-Milligram Levels

The NBL titrimetric method (ferrous ion reduction) of determining uranium has been applied to the 10- and 20-mg. levels. The results are reliable, with precisions and accuracies below 0.1%, provided a few minor modifications in the basic procedure are made.

Titrimetric Determination of Uranium in the 100- to 6000-Microgram Range

The application of the NBL titrimetric method (ferrous ion reduction) to the determination of uranium in the 100- to 6000-μg. range is reported. Under the conditions used, 36 μg. is the lower limit of determination. Recommendations are made for the routine analysis of samples containing these low levels of uranium.

Automatic Determination of Uranium by Ferrous Ion Reduction in Phosphoric Acid and Constant Current Titration with Electrogenerated Vanadium(V)

The NBL method of determining uranium by ferrous ion reduction in phosphoric acid has been modified by substituting titration with electrogenerated vanadium(V) for the dichromate titration. An automatic instrument based upon this procedure is being constructed.

Effect of Added Vanadyl Ion on the Accuracy of the New Brunswick Laboratory Titrimetric Method (Ferrous Ion Reduction) of Determining Uranium

In the NBL titrimetric uranium method (ferrous ion reduction), the use of aged vanadyl sulfate solutions can cause significant errors in the analyses of small amounts of uranium. The routine use of solid vanadyl sulfate reagent is recommended.

Titrimetric Determination of Uranium in Solutions Containing Mercury

A procedure was developed to remove mercuric ion, which interferes with the NBL titrimetric uranium method (ferrous ion reduction), without the use of hydrogen sulfide. Reduction by stannous chloride and filtration of the mercury and mercuric chloride provides a rapid and reliable separation.

Effect of Plutonium on the Determination of Uranium by the New Brunswick Laboratory Titrimetric Method

The effect of plutonium on the NBL titrimetric method of determining uranium by ferrous ion reduction in phosphoric acid was studied briefly. It was found that large amounts of plutonium can give serious negative errors.

Stability of Plutonium Sulfate Tetrahydrate as a Primary Standard: a Ten-Year Evaluation

The stability of plutonium sulfate tetrahydrate, proposed by the New Brunswick Laboratory as a primary chemical standard, has been studied over a 10-year period. The material is stable for at least this time under ordinary storage and handling conditions. The material gains or loses weight under extremes of relative humidities but these changes are reversible.

Preparation and Dissolution of Plutonium Samples in the Nuclear Fuel Cycle

A description of the types of product and scrap materials received at NBL is given. The sampling, shipping, and dissolution of the various samples are discussed.

Heterogeneity of Plutonium Scrap Materials

The heterogeneity of various plutonium scrap materials was demonstrated by carrying out replicate analyses of different scrap samples received at NBL.

The Treatment of Residues from the Dissolution of Plutonium Scrap Materials

Various plutonium scrap materials were dissolved by either 8N nitric acid-0.1N hydrofluoric acid attack or by sodium bisulfate fusion. The fusion procedure gave nearly complete dissolution of the type of samples tested and the insoluble portions contained insignificant quantities of plutonium.

Further Studies on the Anion-Exchange Separation of Plutonium

At NBL, plutonium as plutonium(IV) is separated from other elements by ion exchange prior to its determination by constant-current potentiometry. Additional studies have been made of the separation: the conversion of other plutonium oxidation states to plutonium(IV) by several techniques; the use of different lots of anion-exchange resin, Bio-Rad AG-1; the use of a new resin, Bio-Rex 9.

A Carrier Layer Distillation Method for Refractory Material in Uranium

To increase the sensitivity of the direct emission spectrographic determination of the refractory elements titanium, niobium, and zirconium in uranium materials, the use of the carrier technique was investigated. A mixed carrier of silver chloride and uranium tetrafluoride is proposed.

Comparison of Atomic Absorption and Emission Spectroscopic Determination of Impurities in Uranyl Nitrate

A comparison of atomic absorption and emission spectroscopic results for six impurity elements in uranyl nitrate is presented. Except for an occasional anomalous result, the agreement between the methods is good. The precisions of determination for each element differ appreciably, but one method does not show better precision for all elements.

Simultaneous Determination of Carbon and Sulfur in Uranium Dioxide and Boron

A method for determining carbon and sulfur simultaneously in uranium dioxide or boron, using a high frequency induction furnace and a gas chromatograph, is described.

Tentative Method for the Assay of Boron Trifluoride-Dimethyl Ether

A tentative procedure for the assay of boron trifluoride-dimethyl ether complex is presented involving the precipitation of fluoride with thorium, distillation of methyl borate and titration of boric acid in the distillate.

Determination of Fluoride in Boron by Pyrohydrolysis and a Fluoride-Specific Electrode Measurement

The pyrohydrolysis step in the existing NBL method for determining fluoride in elemental boron has been improved, and the spectrophotometric determination of the separated fluoride has been replaced by a fluoride-specific electrode measurement.

Safeguards Analytical Laboratory Evaluation (SALE) Program

A Safeguards Analytical Laboratory Evaluation (SALE) program has been initiated. The distribution of uranium dioxide samples to the cooperating laboratories has been completed.

A Computer-Controlled Mass Spectrometer Data Acquisition Laboratory

A description of the equipment, programming, and operation of the New Brunswick Laboratory (NBL) computer-controlled mass spectrometer system is given along with information on the performance and reliability.

A Vacuum Lock for a Thermal-Ionization-Source Mass Spectrometer

A vacuum lock for a thermal-ionization-source mass spectrometer has been designed and is now in use. The design is unusual in that a 2-inch gate valve is used as part of the source-isolating system. Pumpdown times have been reduced from 30 min. to less than 3 min. with the vacuum lock.

Solid-State Versions of the Oak Ridge National Laboratory (ORNL) Models Q-2564 and Q-2005 Controlled-Potential Coulometers

Construction of solid-state versions of ORNL Model Q-2564 and Q-2005 controlled-potential coulometric titrators and results obtained are discussed.

APPLICATION OF THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD (FERROUS ION REDUCTION) TO THE PRECISE ASSAY OF URANIUM METAL

A. R. Eberle and M. W. Lerner

The Davies and Gray titrimetric method[1] of determining uranium involving the reduction of uranium(VI) to uranium(IV) by iron-(II) in phosphoric acid, selective oxidation of the excess iron-(II), and titration with dichromate has been modified by the New Brunswick Laboratory (NBL).[2] The vastly improved NBL method, applicable to most sample types, is rapid and reliable, with both precisions and accuracies generally well within 0.1%. In this method, the quantity of uranium taken for analysis is 50 to 250 mg., and the parameters of the recommended procedure, including the volumes and concentration of reagents and the timing of the various reactions, are based upon this amount of uranium(VI) being present at the start.

To obtain a precision and accuracy of 0.01% or lower, it is necessary at the onset to use at least 2- to 5-g. samples. This quantity of uranium(VI) being present at the start of the procedure requires drastic changes in the procedural details, e.g., increasing greatly the quantity of ferrous ion reductant. If, on the other hand, most of the uranium in the dissolved sample could be obtained as uranium(IV), the NBL procedure could be applied with little change. This approach was used for the recommended procedure reported here.

Conditions were found by which large samples could be dissolved with the resulting solutions containing chiefly uranium(IV) and being compatible with the procedure in all other ways. Traces of uranium(VI) in the solution are then reduced in the normal way with the usual quantity of ferrous ion. A change in the final titration involves the initial addition of a weighed quantity of solid primary standard potassium dichromate about 10 mg. less than the required amount and completion of the titration with a standard dichromate solution.

The proposed method is highly precise with a coefficient of variation in the order of 0.005%. The accuracy is assessed by comparing the results shown by NBL dingot uranium with those obtained by other methods. The proposed assay method has three important advantages over other previous high-precision methods: (1) it is extremely rapid once the sample is in solution; (2) it is simple, requiring no expensive equipment; (3) there is no interference from traces of impurity elements such as iron that may interfere in other methods.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus are identical to those described in reference (2) except that solid vanadyl sulfate dihydrate is used instead of the 0.05M vanadyl sulfate.

Procedure

Cut the uranium metal into 1- to 1.5-g. pieces. Pickle the pieces in (1+1) HNO_3, wash with water then acetone, and air dry. Weigh a 4.5- to 5.5-g. sample quickly with a semi-microbalance to $\pm$ 0.02 mg. Correct the weight for buoyancy.

Place the sample in a 400-ml. beaker, add 50 ml. of 85% H_3PO_4, 1 ml. of the standard dichromate solution (to oxidize any reducing substances in the H_3PO_4), and 0.05 ml. (about 1 drop) of 48% HF. Place the uncovered beaker on a steam bath and allow to remain overnight for complete dissolution. Add 10 ml. of (1+1) H_2SO_4 and a magnetic stirring bar, swirl gently to mix well, and cool to room temperature.

Apply the modified NBL titrimetric method as follows. Begin stirring the solution and add 5 ml. of the sulfamic acid solution and then 5 ml. of the ferrous sulfate solution. Allow any precipitate that has appeared to redissolve then wash down the beaker sides with 10 ml. of the HNO_3-molybdate solution. Swirl by hand at this point to continually wet the beaker walls. When the black color produced in the solution disappears, allow the solution to stand without stirring for exactly 3 min. Begin the stirring again and add 100 ml. of water and 75 to 125 mg. of solid vanadyl sulfate. Immediately add a weighed amount of potassium dichromate (corrected for buoyancy and oxidizing power) about 10 mg. less than required to oxidize the uranium(IV). Wash down the beaker sides, insert the platinum and calomel electrodes, and complete the titration with the standard dichromate solution in the usual manner, adding the titrant rapidly to a potential of 490 to 500 mv., waiting about 30 sec. then adding 0.10 ml. increments to beyond the inflection point at 590 mv. (The potential break with the 0.10 ml. increment is 80 to 90 mv. and begins near 530 mv.) Calculate the volume of dichromate solution used from the second-derivative potential data in the usual way and add the quantity of titrant dichromate to the weight of solid dichromate added previously.

RESULTS AND DISCUSSION

The proposed method was evaluated by analyzing NBL dingot uranium metal, long used at NBL as a uranium standard, to which has been assigned a value of 99.972% uranium. A series of 15 analyses gave the results shown in Table 1. Also shown in Table 1 are the values obtained by other methods. The proposed method gives a mean value of 99.973% which compares well with the accepted value. The precision is good, the coefficient of variation having the same order of magnitude as the other high

precision methods. In addition, no correction for certain impurities such as iron is necessary. As with all the modifications of the NBL titrimetric method involving reduction by ferrous ion in phosphoric acid, the procedure is extremely fast after sample dissolution and requires no special equipment other than a pH meter.

TABLE 1

COMPARATIVE HIGH-PRECISION ANALYSES OF NBL DINGOT URANIUM METAL

Method	Analyst	No. of Determinations	Uranium, %	Precision, C.V., %
Proposed	NBL	15	99.973	0.0047
Previous NBL-I[3,4,a]	NBL	5	99.972	0.0028
	NBL	10	99.971	0.0032
	NBS[b]	24	99.972	0.0071
Previous NBL-II[5,c]	NBL	9	99.972	0.006
Voss and Green[6,d]	OR[e]	-	99.973	0.009 (95% CL)
Coulometric, NBS[7,f]	NBS	24	99.972	0.004 (95% CL)
Coulometric, British[8,g]	reference 8	20	99.972	0.005

(All values are based upon an atomic weight of 238.03 and are corrected, when appropriate, for the iron content, and the oxidizing power of the potassium dichromate titrant.)

a. Method involves electrolytic reduction at an amalgamated gold cathode, hydrogen-ion oxidation of uranium(III), and titration with dichromate; the endpoints are determined potentiometrically.

b. Analyses carried out at the National Bureau of Standards by J. K. Taylor and R. A. Paulson, March 1959.

c. Method involves reduction with a Jones reductor, air oxidation of uranium(III), and titration with potassium dichromate with both endpoints determined spectrophotometrically.

d. Method involves reduction with a Jones reductor, titration to the uranium(III)-(IV) endpoint with weak dichromate solution using tungsten and platinum electrodes, then titration with potassium dichromate using platinum and calomel electrodes.

e. Analysis carried out at Union Carbide Corporation, Nuclear Division, by J. C. Barton, March 1959.

f. Method involves the titration of uranium(VI) with electrogenerated titanium(III).

g. Method involves the reduction to uranium(IV) by titanium(III), addition of iron(III), and titration of the resulting iron(II) with electrogenerated cerium(IV).

After the proposed procedure was evaluated, a brief study was made of a procedure involving a dissolution that yields uranium(VI) and the use of large quantities of ferrous ion as mentioned above. With 4- to 5-g. samples, the quantity of ferrous ion needed for the reduction exceeds the solubility of the ferrous sulfate in the H_3PO_4, but with 2-g. samples the required amount can be added. Briefly, the method consists in dissolving the sample in a mixture of 40 ml. of H_3PO_4 and 10 ml. HNO_3. After evaporating off the HNO_3 and dilution with water, 2.4 g. of ferrous sulfate heptahydrate per gram of sample is added and the solution is digested for 1 hr. on a steam bath in the covered beaker. The solution is then cooled, and 5 ml. of (1+1) H_2SO_4, 5 ml. of sulfamic acid solution, 2 ml. of ferrous sulfate solution, and 10 ml. of HNO_3-molybdate solution are added in the order given, followed by the usual steps outlined above.

Five analyses gave a mean value of 99.970% with a coefficient of variation of 0.0039% for the dingot uranium. This value seems to be slightly low but the method appears promising in that the dissolution is very fast when HNO_3 is added to the H_3PO_4. Apparently the 2-g. sample size is adequate for high precision. The identical procedure should be useful to assay uranium dioxide; however, in this case the uranium(IV) obviously cannot be determined along with the total uranium. (See this annual report, p. 10) Additional evaluation of the procedure with uranium dioxide, U_3O_8 as well as the dingot metal may be carried out in future work.

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TITRIMETRIC DETERMINATION OF TOTAL URANIUM AND URANIUM(IV) IN URANIUM DIOXIDE

A. R. Eberle and M. W. Lerner

The procedure described for the precise and accurate determination of uranium in uranium metal[1] has been applied in the present work with little change to the determination of total uranium in uranium dioxide. In the uranium metal procedure, the uranium is dissolved in phosphoric acid to obtain essentially uranium(IV). The New Brunswick Laboratory (NBL) titrimetric method[2] involving reduction to uranium(IV) by ferrous ion in phosphoric acid can then be applied with little modification to the resulting solution. Dissolution procedures that give uranium(VI) are unsatisfactory because the ferrous ion concentration in the reduction step of the NBL titrimetric procedure is insufficient to reduce the large amounts of uranium(VI) obtained from 4- to 6-g. samples. With uranium dioxide samples, the dissolution can be carried out similarly in phosphoric acid containing a small amount of hydrofluoric acid to obtain chiefly uranium(IV). Thus, the procedure is extremely simple and reliable.

It should also be possible to determine the uranium(IV) content of the uranium dioxide by a simplified procedure because no significant oxidation or reduction of the uranium occurs in the dissolution in phosphoric acid.[3] A tentative procedure for this determination is included in the present report. Once the total uranium and uranium(IV) are known, the uranium(VI) can be determined by difference. The uranium(VI) determination is important in the characterization of the oxygen:uranium ratio in reactor-grade uranium dioxide.

EXPERIMENTAL

Reagents and Apparatus

All reagents and apparatus are identical to those described in reference (1).

Procedures

Dissolution of UO_2 Samples. Weigh on a semi-microbalance a 3-g. sample of powder and correct the weight for buoyancy. Transfer the sample to a 400-ml. beaker and add a magnetic stirrer bar, 50 ml. of 85% H_3PO_4, 5 ml. of H_2O and 1 ml. of 48% HF. Heat the mixture in a water bath at 95° to 100°C held on a magnetic stirrer-hot plate and stir constantly. After complete dissolution (about 10 to 15 min.), cool the solution to room temperature.

Determination of Total Uranium. Add to the solution prepared as above, in the order given and mixing thoroughly after each addition by swirling, 5 ml. of H_2O, 5 ml. of H_2SO_4, 5 ml. of 1.5M sulfamic acid, 5 ml. of 1M ferrous sulfate, and 10 ml. of the 8M HNO_3-molybdate reagent. When the black color that develops in the solution disappears, allow the solution to stand for 3.0 min., then add 100 ml. of water and 100 to 125 mg. of solid vanadyl sulfate. Begin the stirring again and add a weighed amount (corrected for purity and buoyancy) of solid primary standard potassium dichromate (NBS-136b) about 10 mg. less than required for the oxidation of the uranium(IV). Wash down the beaker sides, insert the electrodes, and complete the titration with the standard dichromate solution in the following manner. Titrate rapidly to a potential of about 490 mv. (At this point about 0.5 ml. more titrant is required to reach the endpoint.) Stir the solution about 30 sec. and then add the dichromate in 0.10-ml. aliquots, recording the potential after each addition. Continue the titration at least one increment beyond the potential break. Calculate the milliliters of dichromate required by the usual second derivative technique, then calculate the total dichromate consumed.

Determination of Uranium(IV). Prepare in a separate beaker a ferric ion solution by adding in the order given 5 ml. of 1.5M sulfamic acid, 40 ml. of 85% H_3PO_4, 5 ml. of 1M ferrous sulfate and 10 ml. of the 8M HNO_3-molybdate reagent and allowing the solution to stand at least 3 min. after the black color discharges. Add to the sample solution, prepared as in the Dissolution of UO_2 Samples, 5 ml. of H_2O, 5 ml. of H_2SO_4 and the ferric ion solution prepared above. Mix by swirling and allow to stand for 3 min. Add a magnetic stirring bar, 100 ml. of H_2O and 100 to 125 mg. of solid vanadyl sulfate, and titrate as described above for the total uranium.

RESULTS AND DISCUSSION

Six analyses for total uranium were carried out on each of four bottles of uranium dioxide previously analyzed by the NBL titrimetric (ferrous ion reduction) procedure with 200-mg. samples. The results are shown in Table 1. This material is very fine and readily absorbs atmospheric moisture during periods of high humidity. When these analyses were carried out, no difficulty in weighing the samples was observed. A comparison of the two sets of results shows the agreement for the averages to be remarkable. The precision for the procedure presented here is slightly less than that reported for the assay of uranium metal: coefficient of variation of 0.008% versus 0.005%, respectively.

The uranium(IV) content of the UO_2 can also be determined by simply dissolving the UO_2 sample in an identical manner and titrating the uranium(IV) obtained without going through the reduction and oxidation steps. However, when this procedure is followed, the endpoint in the titration is not as sharp as usual despite the presence of the vanadyl ion, and the titration reliability suffers. This behavior is apparently caused by the absence of iron in the solution, since in previous work[2] it was demonstrated that a quantity of either iron(II) or iron(III) is

necessary in the solution for the beneficial effect of the vanadyl ion. Therefore, in the proposed uranium(IV) procedure, iron(III) is added to the sample solution after dissolution. This iron(III) solution is prepared by oxidizing iron(II) as in the conventional procedure with HNO_3-molybdate in the H_3PO_4 medium. With the added iron in the solution being titrated the endpoint is now extremely sharp as usual. The iron(III) is prepared and added in this manner to oxidize any other reducible material present in the sample solution after dissolution so that only uranium(IV) is titrated.

TABLE 1

ANALYSIS FOR TOTAL URANIUM

Procedure	Number of Analysis	Average total Uranium, %	Coefficient of Variation, %
Present Work	24	87.77	0.008
Conventional (200-mg. samples)	44	87.77	0.022

Only a limited amount of work has been done to date on the uranium(IV) determination. Four samples from a fresh bottle of the uranium dioxide were weighed out immediately. Two samples were used for the total uranium and two for the uranium(IV) determinations. No difficulty was observed in weighing these samples. At a later date, four additional samples were taken from the same bottle and some change in weight caused by high humidity was observed on weighing these samples. The results are shown in Table 2. It will be noticed that the results of the first samples for total uranium agree well with the previous analyses, Table 1. On the other hand, the total uranium results on the second set of samples are lower presumably because of moisture pick-up during weighing. The results for the uranium(IV) show somewhat larger differences.

TABLE 2

ANALYSIS FOR TOTAL URANIUM, URANIUM(IV), AND URANIUM(VI)

Sample Set	Uranium, %			Uranium(VI), %
	Total U	U(IV)	U(VI) Calc.	Coulometry[a]
1st	87.768	83.503		
	87.764	83.529		
Average	87.766	83.516	4.25	4.46
2nd	87.744	83.426		
	87.726	83.444		
Average	87.735	83.435	4.30	

a. Controlled-potential coulometry after dissolution in H_3PO_4.

Also shown in Table 2 are the calculated uranium(VI) values along with the average of some uranium(VI) values determined previously by controlled-potential coulometry after dissolution in H_3PO_4. At the present time the difference found in the uranium-(VI) content has not been resolved. More work on the uranium(IV) determination by the present tentative procedure is contemplated in the future. The total uranium procedure is satisfactory at the present time.

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TITRIMETRIC DETERMINATION OF URANIUM AT THE 10- AND 20-MILLIGRAM LEVELS

A. R. Eberle and M. W. Lerner

The New Brunswick Laboratory (NBL) titrimetric method of determining uranium has been shown[1] to give adequate precision and accuracy when 100 to 250 mg. of uranium is taken for the determination. Frequently, however, sample solutions that contain about 1 to 2 mg./ml. of uranium must be analyzed. With the basic NBL procedure, which has a sample volume limitation of 15 ml., the reliability of determining quantities of uranium down to 10 mg. is unknown. Although this type of sample can be analyzed by the "50-ml. procedure",[1] or by the basic procedure after concentration by evaporation when such a step is possible, it was felt worthwhile to establish the conditions necessary for the reliable analysis of sample solutions at these levels.

In the present work, a few minor modifications were found to be necessary to adapt the method to these lower levels. With the proposed changes, the coefficient of variation at both the 10- and 20-mg. level was 0.08%; the accuracy at the 20-mg. level was $-0.015 \pm 0.035\%$ (95% C.L.), at the 10-mg. level, $0.020 \pm 0.048\%$ (95% C.L.).

EXPERIMENTAL

Reagents and Apparatus

The reagents for the reduction of the uranium prior to titration are the same as those given in reference (1) except for the vanadyl sulfate solution.

Vanadyl Sulfate. $VOSO_4 \cdot 2H_2O$.

Potassium Dichromate, 0.0085N and 0.0045N. Dissolve the appropriate quantity of National Bureau of Standards NBS-136b primary standard potassium dichromate, corrected for buoyancy and for purity (99.98%), in 2 l. of water at 25°C.

Standard Uranium Solution, 2 mg./ml. Prepare from NBL dingot uranium metal dissolved in HNO_3 after pickling and weighing. Weigh the final solution made to volume to get a standard solution by weight in addition to volume.

pH Meter. Wide-scale, with platinum and calomel electrodes.

Procedure

Transfer a weighed 5- to 10-ml. aliquot of the standard uranium solution to a 400-ml. beaker. Add 5 ml. of the 1.5M

sulfamic acid, 40 ml. of H_3PO_4 and 1 ml. of the 0.0085N potassium dichromate solution. Mix by swirling carefully. Add 5 ml. of the 1.0M ferrous sulfate solution, swirl the solution and allow to stand for about 1 min. Wash down the beaker sides with 10-ml. of the 8M HNO_3-molybdate reagent, and swirl again to mix thoroughly. When the black color produced in the solution disappears, allow the solution to stand for a timed 3.0-min. period. Add a magnetic stirring bar, 100-ml. of water and from 75 to 125 mg. of solid vanadyl sulfate. Immerse the platinum and calomel electrodes, start the stirring at a rapid rate, and titrate immediately with the standard dichromate solution (0.0085N for the 20-mg. level, 0.0045N for the 10-mg. level) to a potential of about 480 mv. Allow to stand for about 30 sec. with stirring, then continue the titration with 0.10-ml. increments, recording the potential after each addition, to the potential break of 80 to 100 mv. occurring near 530 mv. and moving past 600 mv. Continue the titration at least one increment beyond the endpoint. Calculate the endpoint by the usual second-derivative procedure. Correct the volume of titrant used for the ambient temperature.

RESULTS AND DISCUSSION

Solid vanadyl sulfate reagent is used in place of the usual vanadyl solution[1] because it was found that vanadate ion or some other oxidant slowly appears in the reagent solution upon standing more than a few hours.[2] The quantity of oxidant that is formed in the solution within a day or two does not affect the results when the normal 100 to 250 mg. of uranium is analyzed, but with 10 or 20 mg. of uranium, the effect is clearly seen, with errors of up to -0.5% being obtained. With the solid vanadyl reagent, the error due to the presence of vanadate is insignificant even at the 10-mg. uranium level.

It was also established that the H_3PO_4 contains traces of reducing substances that are not oxidized by the HNO_3-molybdate reagent and give results in some cases 0.5% high in the determination of 20 mg. of uranium. These reducing agents in the H_3PO_4 can be oxidized by a small amount of potassium dichromate prior to the reduction step in the procedure. The oxidized form is not reduced again by the ferrous ion. In the procedure any excess dichromate used for the oxidation is reduced by the ferrous ion and no interference occurs.

Replicate analyses of weighed aliquots of the standard uranium solution are shown in Table 1.

TABLE 1

REPLICATE ANALYSES AT THE 10- and 20-MILLIGRAM LEVEL

Number of Analyses	Uranium, mg.	Coefficient of Variation, %	Accuracy,[a] %
24	20-22	0.083	-0.015 ± 0.035
14	10-11	0.083	+0.020 ± 0.048

a. Relative difference ± 95% C.L.

It is interesting to note that care must be exercised in analyzing volume aliquots of these solutions: pipets calibrated with water may give erroneous deliveries of the uranium solutions. For example, a pipet calibrated with water to deliver 9.990 ml. was found to deliver closer to 9.985 ml. of the uranium solution. This value was determined by analyzing six delivered volumes by the proposed procedure.

REFERENCES

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

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

TITRIMETRIC DETERMINATION OF URANIUM IN THE 100- TO 6000-MICROGRAM RANGE

C. G. Goldbeck

The New Brunswick Laboratory (NBL) method[1] of determining uranium by ferrous ion reduction and dichromate titration is generally used with 100- to 250-mg. samples. Recently, the reliability of the method in determining 10- to 20-mg. quantities of uranium was investigated.[2] In the present work, the application of a scaled-down procedure to still smaller samples was briefly studied.

In order to have sufficient room for the conventional size reference and platinum electrodes, a buret tip, and a magnetic stirrer bar, at least a 50-ml. beaker is needed for the cell. This size beaker can contain about 30 to 40 ml. of final diluted solution in the procedure, and this volume necessitates a scaling-down of the reagent volumes to about one quarter of the usual amounts.

EXPERIMENTAL

Reagents and Apparatus

Sulfamic Acid, 1.5M

Reducing Solution, prepared by adding 400 ml. of 85% H_3PO_4 to 40 ml. of ferrous sulfate solution (280 g. of ferrous sulfate heptahydrate in 1 l. of 10% H_2SO_4).

Oxidizing Solution, prepared by dissolving 4 g. of $(NH_4)_6Mo_7O_{24}$ in 500 ml. of HNO_3, adding 100 ml. of the 1.5M sulfamic acid, and diluting to 1 l.

Diluent, 5% H_2SO_4 containing 0.8 g./l. of vanadyl sulfate per liter.

Potassium Dichromate Solution, 0.01 and 0.03N.

pH Meter, wide-scale, with platinum and Ag-AgCl electrodes.

Micrometer Buret, Gilmont Ultraprecision, 2.5-ml. capacity, with each division equal to 0.001 ml. and a vernier to estimate between divisions.

Procedure

Add 3 ml. or less of sample solution to a 50-ml. beaker. Add 1.25 ml. of the sulfamic acid and begin the magnetic stirring. Add 10 ml. of the reducing solution carefully by pipet into the solu-

tion, avoiding the beaker walls, and allow to mix. Add 2.5 ml. of the oxidizing solution and again mix. Exactly 3 min. after the disappearance of the black color developing in the solution, add 23 ml. of diluent. Titrate immediately and as quickly as possible to a potential of about 580 mv. At this point, add small increments, 0.001 ml. of 0.03N or 0.002 ml. of 0.01N titrant, to a potential break from about 620 mv. to 660 mv.

RESULTS AND DISCUSSION

Replicate determinations were made at levels ranging from 126 to 2530 µg. delivered by volume aliquots of standard uranium solutions, Table 1.

TABLE 1

URANIUM DETERMINATION AT VARIOUS LEVELS

Uranium, µg.	
Taken	Found
126	112, 96, 105, 114, 109
632	619, 616, 636
1265	1265, 1267, 1278
2530	2540, 2527, 2537, 2538, 2514, 2543, 2515

Determinations below the 126-µg. level were attempted. At the 36-µg. level, errors as large as 100% were obtained. Samples at the 12- and 25-µg. levels gave identical results equivalent to about 30 µg. of uranium.

The precision was tested by carrying out replicate determinations of weighed samples, Table 2.

TABLE 2

REPLICATE RESULTS OF WEIGHED ALIQUOTS - 0.01N TITRANT

Uranium Taken, mg.	Titrant Volume, ml.		mg./ml.
2.148	1.798		1.194
2.338	1.957		1.194
2.714	2.270		1.195
1.335	1.121		1.191
1.823	1.529		1.192
0.933	0.783		1.191
		Average	1.193
		C.V., %	0.14

Larger quantities of uranium required 0.03N titrant in order to be able to use the same microburet. A set of 5-ml. volumes (6 mg. uranium) of the same standard uranium solution gave titration values of 1.781, 1.780, 1.780, 1.779, and 1.778 ml. Weighed aliquots gave results similar to those shown in Table 2.

Estimates of accuracy based upon the normality of the dichromate cannot be made because direct blank determinations cannot be carried out. It is known that different lots of H_3PO_4 contain different amounts of a reducing agent that is not oxidized by the HNO_3-molybdate reagent and thus causes positive errors, and that the vanadyl solution may contain vanadate that could cause negative errors. Therefore, it would seem that a standardization of the dichromate titrant under the identical conditions to be used and to include the blank would be the most practical procedure for the analyses of samples at these low levels.

REFERENCES

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

2. Eberle, A. R. and Lerner, M. W., NBL-258 (June 1971), p. 14.

AUTOMATIC DETERMINATION OF URANIUM BY FERROUS ION REDUCTION IN PHOSPHORIC ACID AND CONSTANT CURRENT TITRATION WITH ELECTROGENERATED VANADIUM(V)

C. G. Goldbeck and M. W. Lerner

The New Brunswick Laboratory (NBL) method[1] of determining uranium involving ferrous ion reduction in phosphoric acid, selective oxidation of the excess ferrous ion with nitric acid and molybdenum catalyst, and titration of the uranium(IV) with dichromate has been automated[1] at NBL. Briefly, the automatic instrument consists of a mechanical programmer-timer unit, a Fisher Scientific Company Titralyzer appropriately modified to allow for correct timing of the reagent addition, and associated pumps and reservoirs for the reagent additions.

An improved version of this instrument is now being developed. The improvements consist of the use of an electronic timer which will be more easily adjusted and maintained than the mechanical type and will allow a savings in time for each analysis, and the substitution of constant current titration with electrogenerated vanadium(V) for the dichromate titration. Thus, the buret and the standard solution preparation will be eliminated.

Some studies of the coulometric titration have been made. It has been established that the overall reaction leading to the oxidation of uranium(IV) to uranium(VI) proceeds at essentially 100% efficiency under the conditions shown in Table 1.

TABLE 1

COULOMETRIC TITRATION OF URANIUM(IV) AT CONSTANT CURRENT

Electrodes:	platinum gauze cylinder 5 cm. in diameter and 5 cm. long, or gold expanded sheet cylinder 6 cm. in diameter and 2.5 cm. long
Current:	100 to 300 ma.
Uranium Titrated:	40 to 120 mg.
Medium:	solution containing the uranium(IV) prepared as in the conventional NBL method to which 0.5 g. vanadyl sulfate dihydrate is added.

In the existing instrument, a preselected potential is used as the cut-off point of the titration, and overshooting is prevented by the use of a cup-shaped electrode that promotes a "seeking" action i.e. the titrant is added in smaller amounts as

the endpoint potential is approached. With the new instrument, this "seeking" action is not possible, and overshooting is prevented by stopping the current at an initial preselected potential preceding the endpoint potential and then pulsing the current with about 0.1-sec. increments to the selected endpoint potential. The integrated time is measured. This system has been used successfully in preliminary studies.

A complete report will be issued at a later date.

REFERENCE

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

EFFECT OF ADDED VANADYL ION ON THE ACCURACY OF THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD (FERROUS ION REDUCTION) OF DETERMINING URANIUM

A. R. Eberle and M. W. Lerner

In the New Brunswick Laboratory (NBL) titrimetric method[1] of determining uranium involving the reduction of uranium to uranium-(IV) with ferrous ion in a phosphoric acid medium, vanadyl ion is added to the solution just before titration with dichromate. The vanadyl ion dramatically sharpens the endpoint.

In a recent study[2] of the reliability of the method with 10- to 20-mg. samples of uranium instead of the usual 100 to 250 mg., it was found that the vanadyl sulfate reagent solution appeared to be unstable on standing: negative errors appeared when reagent solutions a few hours old were used. These errors did not appear when the larger sample size was used. Apparently, traces of vanadate ion slowly formed in the solution upon standing. In the present work, a brief study of the vanadyl reagent solution was made.

EXPERIMENTAL

Reagents and Apparatus

All are identical to those listed in reference (2) except for the vanadyl sulfate.

Vanadyl Sulfate Solutions, 5 g. $VOSO_4 \cdot 2H_2O$ per 500 ml.

Procedure

Again, the procedure is identical to that given in reference (2) except for the addition of the vanadyl ion. In the work here, either solid vanadyl sulfate or quantities of the vanadyl sulfate solutions are added.

RESULTS AND DISCUSSION

In initial tests, three solutions of vanadyl sulfate were prepared from the same lot of reagent. One of the three solutions was made with water at 30°C and the prepared solution was held at this temperature for the tests; the other two were prepared and held at room temperature, 25°C. With these solutions, 20 mg. quantities of uranium were determined at various intervals after preparation. Solid vanadyl sulfate, 100 to 125 mg., was used as a control, Table 1. Keeping in mind that the normal error in determining 20 mg. of uranium with the solid vanadyl sulfate is about 0.1%, it can be seen from Table 1 that there was no appreciable effect on using the vanadyl solution up to 24 hours after preparation and storage at room temperature.

TABLE 1

DETERMINATION OF 20-MG. QUANTITIES OF URANIUM WITH VANADYL REAGENT IN SOLUTION AND SOLID FORM

Time After Preparations, hrs.	No. 1	No. 2	No.3 (30°C)	Solid V(IV)
0	+0.12	+0.16	-0.16	-0.09
0.4	-0.04	+0.06	-0.08	-0.07
2.5	-0.30	--	--	-0.06
4.0	-0.16	-0.06	-0.09	-0.08
5.0	-0.26	+0.13	--	+0.06
6.0	-0.06	-0.08	--	+0.10
24	+0.09,-0.17 +0.04, 0.00	--	--	-0.06,+0.09
120	-0.31,-0.07 -0.18,-0.26 -0.25	-0.44,-0.37 -0.17,-0.21	-0.48,-0.51 -0.70,-0.50	+0.16,-0.17

On the other hand, different lots of reagents may well vary in this respect. In a previous test[3] carried out with a different lot of reagent, an error of -0.18% was obtained with a solution used within an hour after preparation, and an error of -0.42% was found after 6 hours. The same vanadyl sulfate used in solid form gave an error less than 0.1%.

Solutions held at 25°C or 30°C gave significant errors after storage for 5 days, Table 1. The 30°C solution caused greater errors as would be expected.

To show that the errors are dependent upon the quantity of vanadyl solution used, tests were carried out in which the volumes of vanadyl reagent solutions aged 5 days were varied from 5 to 20 ml., Table 2. The data indeed do reveal the dependence of the error on the quantity of vanadyl ion solution used and suggest that an oxidant, presumably vanadate ion, is present in the solutions after aging.

To confirm this possibility, the vanadyl solutions were analyzed for vanadate by a spectrophotometric procedure reported by Radcliffe and Parker[4] involving the oxidation by vanadium(V) of N,N′-diphenylbenzidine to a violet product.

The standard curve of the spectrophotometric procedure is prepared by adding 35 ml. of water and 40 ml. of HCl to a 100-ml.

volumetric flask, cooling the solution to room temperature, adding from 0 to 100 μg. of vanadium(V) and 10 ml. of a N,N′-diphenylbenzidine reagent solution (saturated filtered solution in 95% ethanol), and bringing to volume with water. The absorbance, measured at 575 mμ in 1-cm. cells against water as a reference, increases to a maximum within a few minutes and then slowly decreases. The maximum absorbance reading is used; the standard curve is linear.

TABLE 2

DETERMINATION OF 20-MG. QUANTITIES OF URANIUM WITH VARYING AMOUNTS OF AGED VANADYL ION SOLUTIONS USED

Volume of Vanadyl Solution, ml.	Error, %	
	Solution No. 1	Solution No. 2
5.0	-0.08, -0.17 (Av.= -0.13)	-0.02, +0.08 (Av.= +0.03)
10.0	-0.31, -0.07, -0.26, -0.18 -0.25 (Av. = -0.21)	-0.44, -0.37, -0.17 -0.21 (Av. = -0.29)
20	-0.42, -0.42 (Av. = 0.42)	-0.61, -0.62 (Av. = 0.62)

The vanadium(V) content of the vanadyl solutions was measured as described for the standard curve preparation. Freshly prepared and aged solutions gave the data shown in Table 3 for vanadate and the uranium equivalent. The vanadate content can be seen to increase slowly on standing.

TABLE 3

ANALYSIS OF VANADYL SULFATE SOLUTIONS FOR VANADIUM(V)

Vanadyl Solution	Preparation and Storage Temp., °C	Age of Solution, hrs.	Vanadium(V), mg./10 ml.	Uranium Equivalent, mg.
A	28	0	0.002	0.005
		1	0.002	0.005
		4	0.003	0.007
		26	0.007	0.016
		96	0.024	0.056
		120	0.027	0.063
B	25	28 days	0.086	0.201
C	25	29 days	0.088	0.206
D	32 (5 days), then 25	22 days	0.116	0.271

Table 4 presents the data obtained by analyzing 10 and 20 mg. of uranium by the NBL titrimetric procedure in which 10-ml. aliquots of the vanadyl solution D (Table 3) were used. The errors found were then compared to the errors calculated from the vanadate(V) content of the vanadyl solution. The agreement between the actual and calculated errors are good.

TABLE 4

ERRORS IN ANALYZING URANIUM WITH AGED VANADYL SOLUTION D

Uranium Taken, mg.	Error, %	
	Found by Titration	Calculated from U(V) Content
10.031	-2.77	-2.70
20.933	-1.34	-1.29

A final series of tests was made to determine the minimum quantity of uranium that must be taken for analysis to keep the error from the use of 5-day old vanadyl reagent solution to less than 0.1%, Table 5. Extrapolation of the data indicates that at least a 50-mg. sample must be used for this particular lot of vanadyl sulfate. Since the lots of reagent appear to be somewhat variable, it is probably best to use at least 100 mg. of uranium with reagent solutions up to 5-days old. It is much better, of course, to use the solid reagent as is now specified for the NBL titrimetric method.

TABLE 5

ERRORS FOUND WITH 5-DAY OLD REAGENT SOLUTIONS AND VARIABLE URANIUM QUANTITIES

Uranium, mg.	No. of Tests	Average Error, %
10	4	0.56
20	4	0.30
40	4	0.12

REFERENCES

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

2. Eberle, A. R. and Lerner, M. W., NBL-258 (June 1971), p. 14.

3. Eberle, A. R. and Lerner, M. W., unpublished data, 1970.

4. Radcliffe, N. C. and Parker, J. R., Anal. Chim. Acta, 52, 9 (1970).

TITRIMETRIC DETERMINATION OF URANIUM IN SOLUTIONS CONTAINING MERCURY

A. R. Eberle and M. W. Lerner

Uranium determination at the New Brunswick Laboratory (NBL) is accomplished by an improved version of the method of Davies and Gray.[1] In the New Brunswick Laboratory (NBL) modification[2] of this procedure, vanadyl ion is added before the titration. The presence of the vanadyl ion makes the endpoint extremely sharp and permits potentiometric titration.

Although Davies and Gray reported that mercuric ion (200 mg. of mercuric nitrate) did not interfere in their procedure, the presence of appreciable quantities of mercury in dissolver solutions received by NBL for analysis was found to have a serious detrimental effect on the NBL potentiometric procedure. The initial potentials were abnormal and the endpoints were very poor. These samples required the prior removal of mercury as the sulfide before the titrimetric procedure could be applied.

A study carried out with standard uranium solutions to which mercury was added revealed that mercuric ion indeed did not interfere seriously with the indicator titration although the blanks appeared to be high and rather variable. As before, the potentiometric titration was rendered useless by the mercury. Therefore, two approaches could be made with solutions containing mercury. The indicator titration (with added vanadyl ion) could be relied upon and the difficulties of the blank resolved by further work, or the mercury could be removed and the potentiometric titration, that ordinarily has no blank problems, applied.

In the present work, the latter approach was used and a substitute was sought for the sulfide separation. The sulfide procedure is time-consuming in that a 4- to 8-hr. digestion period is necessary to obtain a filterable precipitate, and additional evaporation and fuming steps are subsequently needed. In addition, the desire to avoid the use of hydrogen sulfide is always present.

Electrolysis on a platinum cathode removed the mercury efficiently in exploratory studies, but the procedure was slow and did not lend itself well to multiple analyses. A more satisfactory method was found to be the reduction of the mercury(II) with stannous chloride in the presence of hydrochloric acid, and filtration of the mercurous chloride or the elemental mercury. The filtrate is evaporated after the addition of sulfuric acid and, after oxidation of the excess stannous tin with dichromate, the NBL titrimetric procedure is applied with no difficulty.

EXPERIMENTAL

Reagents and Apparatus

The reagents and apparatus for the titration are given in reference (2).

Stannous Chloride Solution, prepared by dissolving 1 g. of $SnCl_2 \cdot 2H_2O$ in 50 ml. of HCl. The mixture is heated to near boiling to obtain a clear solution, then it is cooled to room temperature.

Filter Paper Pulp, prepared by disintegrating Whatman No. 41 filter paper in HCl, diluting the mixture with water and filtering, and washing the pulp free of acid with water.

Funnel, Fisher Filtrator, porcelain, for 11-cm. filter paper.

Bell Jar, to accomodate a 400-ml. beaker and the Fisher Filtrator funnel. (This bell jar is used for vacuum filtration because the Fisher Filtrator will not hold a 400-ml. beaker.)

Procedure

Transfer a weighed aliquot of the sample solution containing from 100 to 150 mg. of uranium to a 400-ml. beaker. Add 10 ml. of $HClO_4$ and evaporate the solution to strong fumes. Cool and dissolve the salts in about 50 ml. of water. Heat the solution to near boiling and add 5 ml. of the stannous chloride solution. Filter the precipitate, using vacuum, on the Fisher Filtrator funnel fitted with a Whatman No. 42 paper plus a quantity of the filter pulp to fill about one-third of the funnel. Wash the precipitate, paper and pulp thoroughly with about 150 ml. of hot water, collecting the filtrate and washings in a 400-ml. beaker. Add 2 ml. of H_2SO_4 and evaporate the solution on a hot plate or overnight on a steambath. Dissolve the salts in 10 ml. of water, add 1 ml. of 1% potassium dichromate solution and wash down the beaker sides with 40 ml. of H_3PO_4. Proceed with the NBL titrimetric method in the usual manner.

RESULTS AND DISCUSSION

Effect of Mercury. Either mercuric or mercurous mercury was added to standard uranium solutions, and analyses were carried out by (1) the original Davies and Gray indicator procedure; (2) the NBL potentiometric procedure; (3) the Davies and Gray procedure modified by the addition of the vanadyl ion, Table 1.

The data in Table 1 indicate that the effect of mercury is different in the two types of titrations, indicator or potentiometric. Potentiometric titrations fail completely, whereas indicator titrations apparently can be used even though the blank values appear to be high and variable. The vanadyl ion improves the indicator endpoint even in the presence of mercury. Fuming the solution first with $HClO_4$ apparently lowers the blank.

TABLE 1

EFFECT OF MERCURY ON ORIGINAL AND MODIFIED DAVIES AND GRAY PROCEDURES

Method	Mercury Added, mg.	$K_2Cr_2O_7$, ml. Required	Found	Difference	Notes
Davies and Gray	0	34.55	34.85	+ 0.30	--
	Hg(II),200	35.15	35.48	+ 0.33	--
	Hg(I), 168	34.89	35.52	+ 0.63	--
NBL[a]	0	35.251	35.254	+ 0.003	Sharp endpoint
	Hg(II),200	35.48	--	--	No endpoint
	Hg(I), 168	35.31	--	--	No endpoint
Davies and Gray	0	35.23	35.87	+ 0.64	V(IV) added - sharp endpoint
	Hg(II),200	36.09	36.60	+ 0.51	V(IV) added - sharp endpoint
Davies and Gray[b]	0	36.60	36.85	+ 0.25	Solution fumed with $HClO_4$;
	Hg(II),200	35.38	35.53	+ 0.15	V(IV) added.

a. Davies and Gray reagents were used: in oxidation step, 5 ml. of 4M HNO_3-0.15M sulfamic acid-0.4% ammonium molybdate instead of 10 ml.of 8M HNO_3-0.15M sulfamic acid -0.4% ammonium molybdate.

b. NBL reagents used.

On the basis of the data in Table 1, attempts were made to analyze mercury-containing dissolver solutions with the indicator titration procedure ($HClO_4$ fuming and V(IV) added). The results were as much as 0.5% in error presumably because of the inability to determine the correct blank value. Since dissolver solution samples contain quantities of aluminum nitrate, synthetic solutions containing 150 mg. of uranium plus 5 g. of aluminum nitrate nonahydrate and 200 mg. of mercuric ion as the nitrate were prepared and analyzed. The endpoint of the titration was now very poor and could only be estimated with results > 10% in error. These synthetic solutions contained much more mercury than the dissolver solutions. Apparently then, while the mercury does not appear to interfere greatly in simple uranium-mercury solutions, its presence in actual sample solutions containing aluminum can cause serious

interference even if the indicator titration is used. For this reason, it was decided to depend at the present time on a separation procedure.

Tolerance of Potentiometric Titration to Mercury. To estimate how complete the mercury removal must be, samples containing known amounts of uranium and aluminum and increasing quantities of mercury, both in a nitric acid and in a sulfuric acid medium, were titrated by the NBL titrimetric method, Table 2. The data indicate that in a nitric acid system, at least 5 mg. can be present. In a sulfuric acid solution, this 5-mg. quantity will cause an appreciable error. Since many samples received are prepared as a sulfuric acid solution, it appears that the separation must be essentially complete.

Table 2

TOLERANCE OF POTENTIOMETRIC TITRATION TO MERCURY

Medium[a]	Mercury(II), mg.	Uranium, mg. Present	Uranium, mg. Found	Error, %
10% HNO_3	0	85.064	85.109	+ 0.05
	2.1	83.973	84.012	+ 0.04
	5.0	84.116	84.099	- 0.02
	10.4	83.435	83.696	+ 0.31
	20.8	83.959	83.370	- 0.70
10% H_2SO_4	0	81.862	81.850	- 0.01
	5.0	82.746	83.041	+ 0.36
	5.0	81.925	82.451	+ 0.63
	10.0	80.101	80.483	+ 0.48
	20.0	83.698	85.102	+ 1.68

a. Solutions contained 5 g. $Al(NO_3)_3 \cdot 9H_2O$.

Removal of Mercury by Electrolysis. The removal of mercury by electrolyses was studied briefly. Nitric acid (2%) solutions containing 500 mg. of mercury and 5 g. of aluminum nitrate nonahydrate plus known amounts of uranium were electrolyzed for 1 hr. at 8 volts and 2.5 amps. with a platinum gauze cathode. The solutions were then evaporated to dryness, the residues taken up in 10 ml. of 10% HNO_3 and the resulting solutions analyzed by the potentiometric procedure, Table 3.

TABLE 3

REMOVAL OF MERCURY BY ELECTROLYSIS ON PLATINUM

Mercury(II), mg.	Uranium, mg. Present	Found	Error, %
500	62.741	62.698	- 0.07
500	83.782	83.928	+ 0.17
510	82.312	82.425	+ 0.14

The separation can be seen to give reasonably good results. It could be used for an occasional sample, but it is not well suited for multiple analyses. In addition, the slight but significant attack on the platinum cathode is another disadvantage. Other electrodes were not tested. Removal of the mercury by plating on copper or zinc sheet or shot was too incomplete with reasonable quantities of metal.

Reduction with Stannous Chloride. The proposed procedure was tested with synthetic uranium-aluminum solutions containing from 47 to 155 mg. of mercury(II) with satisfactory results, Table 4. The filtration as described is rapid and apparently complete. The separation is perhaps a little faster than the hydrogen sulfide precipitation in actual working time but it is much faster in elapsed time since the sulfide procedure requires a 4- to 8-hr. digestion, an evaporation and a fuming step. In the proposed procedure, no digestion or fuming steps are needed.

TABLE 4

ANALYSES OF SYNTHETIC SOLUTIONS[a] BY THE PROPOSED PROCEDURE

Mercury(II), mg.	Uranium, mg. Present	Found	Error, %
47	146.24	146.10	- 0.10
50	91.818	91.773	- 0.05
52	120.13	119.99	- 0.12
71	103.84	103.79	- 0.05
72	106.53	106.52	- 0.01
99	122.98	122.91	- 0.06
102	102.33	102.41	+ 0.08
105	168.92	168.87	- 0.03
140	100.90	100.85	- 0.05
155	89.853	89.837	- 0.02

a. Aliquots contained indicated quantities of mercury and uranium plus 3 g. $Al(NO_3)_3 \cdot 9H_2O$; solutions fumed strongly with 10 ml. $HClO_4$ before analysis.

Analyses were made of actual dissolver sample solutions containing mercury that were also analyzed by the hydrogen sulfide procedure, Table 5. The agreement is good for many samples. For most of the other samples, the proposed procedure appears to give slightly higher values. This fact suggests that the sulfide precipitate drags down traces of uranium. The data in Table 4 indicate that coprecipitation is not a problem in the proposed procedure.

TABLE 5

ANALYSES OF DISSOLVER SOLUTION BY HYDROGEN SULFIDE AND BY PROPOSED PROCEDURE

Uranium, mg./g.		Difference of Averages, %
Hydrogen Sulfide[a]	Stannous Chloride	
18.88, 18.87	18.90	+ 0.08
15.55, 15.53	15.56	+ 0.13
18.67, 18.68	18.69	+ 0.08
16.66, 16.66	16.69	+ 0.18
18.66, 18.86	18.87	+ 0.05
19.82, 19.84	19.89	+ 0.30
14.49, 14.49	14.48	- 0.07
12.30, 12.33	12.27	- 0.36
14.43, 14.45	14.44	0.00
17.09, 17.11	17.11	+ 0.06
45.64, 45.66	45.63	- 0.04
77.31, 77.24	77.57, 77.53	+ 0.36
80.12, 80.10	80.28, 80.34	+ 0.25
84.92, 85.15	85.13	+ 0.10
72.55, 72.76	72.80	+ 0.21
82.53, 82.84	82.86	+ 0.22
86.40, 86.59	86.89, 86.89, 86.87	+ 0.44
51.77, 51.84	51.88	+ 0.14
45.45, 45.63	45.71, 45.66	+ 0.32
42.66, 42.64	42.80, 42.80	+ 0.35
48.16, 48.19	48.18, 48.18	0.00
50.94, 50.92	50.88, 50.87	- 0.11
54.38, 54.25	54.56, 54.42	+ 0.31

a. Suitable aliquot of $HClO_4$ solution diluted to about 100 ml., the solution gassed, the precipitate digested overnight and filtered, the filtrate evaporated and fumed before analysis.

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EFFECT OF PLUTONIUM ON THE DETERMINATION OF URANIUM BY THE NEW BRUNSWICK LABORATORY TITRIMETRIC METHOD

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

The New Brunswick Laboratory (NBL) titrimetric method of determining uranium,[1-3] an improved version of the method first described by Davies and Gray,[4] requires no prior separations from most elements. It has been applied[3] successfully to uranium-plutonium solutions containing as much as 20% Pu on a uranium basis. In the present work, a brief study was made of the effect of higher concentrations of plutonium.

EXPERIMENTAL

The reagents, titration unit and procedure are as described previously.[3] Synthetic solutions of uranium-plutonium were prepared by mixing weighed portions of standard plutonium solutions made from high-purity (99.9%) plutonium metal and standard uranium solutions made from National Bureau of Standards 950a U_3O_8.

RESULTS AND DISCUSSION

Analyses were made of solutions containing from 0 to 192 mg. of plutonium and 153 to 273 mg. of uranium, Table 1. As in the previous tests,[3] it is clear that up to 64 mg. of plutonium has no effect on the determination of about 250 mg. of uranium. Most samples of uranium-plutonium received at NBL contain no more than this quantity of plutonium per aliquot taken for analysis.

However, larger quantities of plutonium can give negative errors. Inspection of the data reveals that the magnitude of the error depends apparently on the amount of plutonium as well as the total quantity of uranium plus plutonium. This fact suggests that in these cases the quantity of ferrous ion in the reduction step of the procedure is insufficient for complete reduction of the uranium in the alloted time. Studies of this factor, along with the associated variables connected with the oxidation step, are planned in future work.

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TABLE 1

EFFECT OF PLUTONIUM ON URANIUM DETERMINATION

Plutonium Added, mg.	Uranium, mg. Added	Uranium, mg. Found	Relative Difference, %
0	232.46	232.44	-0.01
0	273.72	273.53	-0.07
0	268.50	268.40	-0.04
0	269.79	269.88	+0.03
64	251.79	251.83	+0.01
64	260.07	259.99	-0.03
128	153.57	152.95	-0.40
128	198.63	198.33	-0.15
128	179.03	177.83	-0.68
192	280.97	274.14	-2.49
192	232.09	223.11	-3.87
192	266.65	262.34	-1.61

STABILITY OF PLUTONIUM SULFATE TETRAHYDRATE AS A PRIMARY STANDARD: A TEN-YEAR EVALUATION*

C. E. Pietri and A. W. Wenzel

Plutonium sulfate tetrahydrate, $Pu(SO_4)_2 \cdot 4H_2O$, has been proposed[1] by the New Brunswick Laboratory (NBL) as a primary chemical standard for plutonium. A previous study[1] of this compound indicated that it was stable for up to 28 months when stored in screw-capped glass bottles and was essentially unaffected by relative humidities (R.H.) of 17 to 75%.

Because of the possible long-term susceptibility to radiolytic decomposition of the water of crystallization, and because it was considered important to learn the effects of extremes of humidities (< 0.1% and 95% R.H.), the stability tests mentioned above were continued and expanded. The tests were structured to disclose the magnitude and reversibility of any weight changes caused by changes in humidity together with any possible change in stoichiometry. The plutonium content of several lots of plutonium sulfate was determined periodically at 32-, 63-, 75-month, and 10-year periods under the same conditions as were used previously, and when held at relative humidities of < 0.1% and 95% for short periods of time. Any change in plutonium concentration would be indicative of the stability of the compound.

The data indicate that plutonium sulfate tetrahydrate is stable under ordinary storage and handling conditions for at least 10 years. Although the material gains weight on exposure to high humidity and loses weight at very low humidity, the changes are readily reversible on re-exposure to air with normal levels of humidity. A detailed account of this study has been accepted for publication in Talanta.

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* Presented at the 14th Conference on Analytical Chemistry in Nuclear Technology, October 12-15, 1970, Gatlinburg, Tennessee.

PREPARATION AND DISSOLUTION OF PLUTONIUM SAMPLES IN THE NUCLEAR FUEL CYCLE*

C. E. Pietri

Although the basic methods of dissolving plutonium materials have been adequately summarized in recent publications,[1-3] a description of the handling of plutonium samples from the standpoint of an analytical laboratory dedicated to precise and accurate analyses should be available. In the present report, the general techniques used by the New Brunswick Laboratory (NBL) are described.

Many sample types including both product and scrap materials are received by NBL for analysis, Table 1.

TABLE 1

PLUTONIUM SAMPLES RECEIVED BY NEW BRUNSWICK LABORATORY

Product Materials	Scrap Materials
Pu metal and binary alloys	Floor sweeps
U-Pu-Mo	Calcined ash
PuO_2	Brick residues
PuO_2-UO_2	Chemical waste
(Pu-U)C	Crucible-mold waste
$Pu(NO_3)_4$ solution	

The product materials are generally from fuel element fabrication and ordinarily present little difficulty in sampling and dissolution. The scrap materials, described in more detail below, cause endless problems. The two basic methods of dissolving both types of materials are acid digestion with hydrochloric acid or, more often, a mixture of nitric and hydrofluoric acid, and fusion with sodium bisulfate. Frequently both methods must be used for complete dissolution.

Dissolution Procedures

Only the details of the HNO_3-HF attack and the bisulfate fusion are given below. Other procedures involving direct acid attack are straightforward or are combinations of these attacks.

* Presented at the 14th Conference on Analytical Chemistry in Nuclear Technology, October 12-15, 1970, Gatlinburg, Tennessee.

HNO_3-HF Attack. To a sample weighing 1 g. or less in a teflon beaker add 50 ml. of 8N HNO_3 and 1 drop of 48% HF and swirl. Cover the beaker and heat the mixture at 90°C, replenishing the drop of HF about once an hour, until dissolution is complete or the action stops.

$NaHSO_4$ Fusion. Grind a quantity of material in a Diamonite mortar and place a sample weighing 1.5 g. or less in a platinum dish. Mix the sample intimately with 18 g. of $NaHSO_4$, fuse at 600°C for 15 to 20 min., swirl the melt and heat again for an additional 5 min.

Product Materials. The specific dissolution methods commonly used for product material are shown in Table 2.

TABLE 2

PRODUCT SAMPLE TREATMENT

Sample	Dissolution Method
Pu metal, Pu-Ga, Pu-Al	6N HCl (cold) or 18N H_2SO_4 (hot)
U-Pu-Mo	3N HCl-8N HNO_3-0.1N HF
PuO_2, PuO_2-UO_2	8N HNO_3-0.1N HF
PuO_2 (high-fired)	$NaHSO_4$ fusion
(Pu-U)C	Ignition plus 8N HNO_3-0.1N HF or $NaHSO_4$ fusion; 6N HCl plus fusion

Plutonium metal in the form of massive pieces such as rods, chunks, or pins are scraped first with tool steel or electropolished in 20% sodium carbonate solution to remove surface oxide. Metal pieces are cut with heavy-duty wire cutters with hardened tool steel edges. Turnings or chips must be electropolished to remove oxide but in some cases the deeply corrugated surface of turnings makes it impossible to obtain a clean oxide-free surface. In addition, electropolishing of small turnings less than 100 mg. in weight may use up most of the sample. After the sample has been cleaned, it is placed in a volumetric flask and dissolved in cold (1+1) HCl in an ice-bath or in hot 1:1 H_2SO_4. Volumetric flasks are convenient because their tall form prevents loss of sample from effervescence during the dissolution. If the (1+1) HCl is kept below 5°C, if less than 5 g. of metal is used and if a minimum of about 20 ml. of acid solution is used, little oxide forms during the dissolution process. If some oxide forms, it is easily dissolved in 8N HNO_3-0.1N HF. Some oxide forms with the (1+1) H_2SO_4 treatment but it dissolves readily by heating the acid solution to light fumes. Plutonium-aluminum or plutonium-gallium alloys are treated similarly.

Uranium-plutonium-molybdenum alloys are cleaned by the procedures described for plutonium metal, and are dissolved in a mixture of 3N HCl-8N HNO_3-0.1N HF by heating. With fuel elements clad with stainless steel, the cladding is mechanically peeled off before the dissolution treatment.

Plutonium oxide materials received by NBL fall into three categories: low fired (< 800°C); high-fired (> 800°C); low-fired hygroscopic. The low-fired material is dissolved readily in hot HNO_3-HF while the high-fired is best dissolved by sodium bisulfate fusion at 600°C. Pellets or coarse powders are ground to a fine powder for the fusion dissolution. Hygroscopic oxide must be sampled in a dry atmosphere with a dewpoint less than -10°C, or better, in exactly the same environment as it was prepared. The effect of the different dissolution procedures on the analysis of refractory plutonium oxide is shown in Table 3.[4]

TABLE 3

DISSOLUTION OF REFRACTORY PLUTONIUM OXIDE

Treatment	Remarks	Pu Recovery, %
HNO_3	large residue - ignored	99.13 ± 0.18
HNO_3 + HF	slight residue - ignored	99.87 ± 0.05
HNO_3 + HF plus $NaHSO_4$ fusion	slight residue fused	99.98 ± 0.04
$NaHSO_4$ fusion	no residue	100.01 ± 0.04

Mixed oxides are treated like plutonium oxide: hot HNO_3-HF attack, or bisulfate fusion if the acid treatment fails.

Plutonium-uranium carbide samples can be worked up in several ways. In many cases they are simply ignited at 700° to 800°C and the oxides dissolved by the acid attack or fusion as described above. Finely-divided pyrophoric samples are sampled in an inert atmosphere in a covered platinum dish, allowed to react in air, then finally dissolved as described above. Finally, the carbide can be dissolved directly in (1+1) HCl and any residue fused with bisulfate.

Plutonium nitrate solutions present both shipping and sampling problems. NBL has found that the best container for shipment is a sealed glass ampoule. Glass or polyethylene bottles with "poly-seal" screw cap enclosures have been used. Plutonium nitrate solutions appear to attack and permeate polyethylene bottles if stored for more than one week under some conditions. Of course, "green" solutions containing appreciable amounts of plutonium(VI) should not be shipped because pressure build-up may occur. Plutonium(IV) solutions in 8N HNO_3 are much more stable. Studies[5] at

NBL have shown that these solutions can be stored in sealed glass ampoules for at least 21 months with no change in concentration or an unsafe build-up of pressure. After 21 months the increase in pressure is only about 9% of the rated bursting pressure for thin-walled ampoules. Some laboratories freeze the solution to a solid with liquid nitrogen or dry ice-tetrachloroethane mixture before opening the ampoules in order to minimize pressure problems. At NBL, this precaution has not been necessary for most samples, but occasionally pulverized dry ice alone has been used and found to be superior. The use of liquid nitrogen may cause the ampoule to crack or burst under some conditions.

Nitrate solutions can be sampled by taking aliquots directly from the ampoule or bottle, or, if the shipper has an accurate measurement of the volume or weight of solution, by diluting the entire sample and then taking aliquots. In the latter technique, any error due to a volume or weight change in the solution is minimized. Sample bottles that have leaked are rejected. Also rejected are solutions in plastic bottles that have developed precipitates because it has been found that reliable results cannot be obtained in these cases despite tedious efforts to recover and redissolve the insolubles.

The best sampling procedure an analyst can ask for is that the shipper takes a valid sample and packages it properly. Plutonium nitrate solutions have been discussed briefly above. The handling of metal, alloy, and oxide samples warrant some remarks.

It is far better to seal a clean piece of metal or alloy in a dry, inert gas atmosphere in a glass ampoule than to have to clean highly oxidized pieces. It is notable how well the National Bureau of Standards plutonium metal standard that was packaged by Los Alamos Scientific Laboratory has stood up over the years.

Hygroscopic plutonium oxide should be packaged in glass bottles and screw caps with plastic liners for shipment. The bottles should be oven-dried thoroughly and placed in the same atmosphere as the sample to equilibrate. After filling and capping the bottle, one should wrap plastic tape around the neck to ensure that the cap does not loosen. When it is practical, the use of sealed glass ampoules may be even better. Generally, glassware should be used for shipment of solid samples because polyethylene or other plastic material can contaminate the samples by abrasion.

Scrap Materials. The types of scrap received at NBL for analysis, along with the dissolution method for each type are shown in Table 4.

Brief descriptions of these materials can be given. "Floor sweeps" consist of product materials mixed with other oxides, metals, carbonaceous materials, nuts, bolts, turnings, oils, plastics, fibers, etc. Dissolution of these materials is tedious, requiring three to five times more work than it takes for product materials.

TABLE 4

SCRAP MATERIAL TREATMENT

Floor sweeps Calcined ash Chemical waste	8N HNO_3-0.1N HF leach plus fusion of insolubles; $NaHSO_4$ fusion alone.
Brick residues	$NaHSO_4$ fusion
Crucible-mold waste	Ignition followed by 8N HNO_3-0.1N HF attack or $NaHSO_4$ fusion

"Calcined ash" is similar to "floor sweeps" but is generally high-fired (> 1000°C). These materials are dissolved as described for "floor sweeps."

Brick residues are scraping from furnaces and consist of oxides of aluminum, magnesium, calcium and iron, plus silica. The preferred treatment is fusion; any residue remaining contains only negligible amounts of plutonium.[6]

"Chemical wastes" are laboratory chemicals or their decomposition products and may contain organic dyes and various oxides. Dissolution is carried out as described for "floor sweeps."

"Crucible and mold waste" is similar to "floor sweeps" but contains carbon from the graphite molds and crucibles used in casting operations. The carbon is removed by ignition at 900°C prior to the HNO_3-HF treatment or bisulfate fusion.

These scrap samples present difficulties to an analytical laboratory primarily because of the sampling problem. It is obvious that the shipper not only is responsible for maintaining the integrity of the sample, but he must also be aware of the possible errors due to poor sampling. Unfortunately, many suppliers are either unaware of or ignore to some extent this factor. Many samples received by NBL are grossly non-homogeneous.[7] In most cases this situation obviously cannot be helped, but from the comparative data obtained it is clear that the average sample is far from representative. The work of homogenizing this type of sample after receipt by calcining and blending, and then of quartering or sampling with splitters is lengthy and tedious. Moreover, the precise analysis of this blended sample gives results that have little meaning.

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HETEROGENEITY OF PLUTONIUM SCRAP MATERIALS

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

Obtaining a valid sample for analysis from a bulk sample is of prime importance in any analytical procedure: the best analysis is no better than the reliability of the sample taken. Plutonium scrap materials present serious sampling problems because of the general heterogeneity of the materials. In the present study, the magnitude of the error due to sampling is demonstrated by replicate analysis of various scrap samples received at the New Brunswick Laboratory (NBL).

RESULTS AND DISCUSSION

Nine routine inventory samples of a variety of scrap materials such as plutonium oxide and plutonium oxide-uranium oxide mixed with metal turnings, plastic, fibers, etc., were subsampled, fused with sodium bisulfate[1] and then assayed by the NBL method.[2,3] The subsamples were simply grab samples taken after mixing the sample in the container. Eight of the samples were subsampled into roughly equal portions until the original samples were exhausted. The results are shown in Table 1 along with a calculated average.

TABLE 1

REPLICATE ANALYSES OF PLUTONIUM SCRAP SAMPLES

	Plutonium, %		
Material	Plant Estimate	NBL Analyses	Average
Sludge	5.7	0.51,3.0,0.32,3.3,3.1	2.0
Scrap	1.3	0.45,1.04,1.18,1.37,0.39	0.89
Floor sweeps	18	4.3, 8.9, 3.9, 10.5	6.9
Sludge	13	4.1, 6.8, 6.2, 3.7	5.2
Floor sweeps	13	29.4,31.2,32.9,28.8,19.0	28.3
Scrap	25	2.6, 3.0, 2.8	2.8
Scrap	45	10.7, 6.8, 5.4, 6.1	7.3
Floor sweeps	15	4.1, 8.7, 3.2	5.3
Floor sweeps[a]	22	17.8, 17.4	-

a. Sample not completely consumed by subsampling.

It is clear that the subsamples from a heterogeneous sample of the type analyzed here can differ in plutonium content by a factor of 10. Even if the entire sample were taken for analysis or efficiently homogenized before subsampling, the results would not agree with the plant estimate. This fact suggests that the plant samples were not representative of the bulk samples.

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THE TREATMENT OF RESIDUES FROM THE DISSOLUTION OF PLUTONIUM SCRAP MATERIALS

C. E. Pietri

Among the plutonium scrap samples that are difficult to dissolve are the following:

1. brick fines, containing large amounts of silica plus oxides of iron, aluminum, magnesium, calcium, and other elements;

2. crucible leach sludge, containing large amounts of graphite and various oxides;

3. chemical waste, containing various oxides, organic compounds, and laboratory reagents and their degradation products;

4. grinder sludge, containing silicon carbide and cutting oils.

In the present work, a brief study was made of the dissolution of these materials, comparing the two dissolution procedures normally used at the New Brunswick Laboratory (NBL) to dissolve plutonium samples: acid attack with 8N nitric-0.1N hydrofluoric acids; fusion with sodium bisulfate. The plutonium content of the small residues remaining from the more efficient bisulfate fusion treatment was investigated.

Procedure

The dissolution procedures have been described in recent reports.[1,2]

RESULTS AND DISCUSSION

In one series of tests, the four types of samples were subsampled by taking grab samples after mixing. Duplicate subsamples were treated by the acid attack; other duplicates were fused with the bisulfate, Table 1.

The acid attack generally leaves large amounts of dark residues, while the fusions give only small quantities of light-colored residues. Although the assay values are quite variable because of the heterogeneous nature of the samples, it appears that slightly higher results are obtained with the fusion attack and that the amount of residue does not clearly account for the high or low value for the assay in either dissolution procedure.

TABLE 1

DISSOLUTION OF PLUTONIUM SCRAP MATERIALS

Material	Plutonium, %			
	8N HNO_3-0.1N HF	(Residue)	$NaHSO_4$	(Residue)
Brick fines	10.7	large	11.0	very small
	9.1	large	8.7	very small
Crucible leach sludge	3.3	medium	4.1	small
	3.1	medium	3.6	small
Chemical waste	5.4	small	3.8	small
	8.7	large	8.4	small
Grinder sludge	41.7	large	41.9	very small
	41.5	medium	41.5	small

To dissolve the insolubles left by the acid attack, it is necessary to filter the residue and fuse it with sodium bisulfate. Any insolubles left after this bisulfate fusion must then be fused with sodium carbonate. Since this procedure is very lengthy, the possibility of ignoring the smaller residue left in the original sodium bisulfate fusion procedure was studied.

The residues from the initial fusion treatment of each of the four types of samples were filtered, fused with sodium carbonate, the melt taken up in dilute nitric acid, and aliquots taken for alpha counting, Table 2. It can be seen that the greatest concentration in the residues amounts to < 0.03% on the sample basis. Considering that the normal precision of analysis is 0.05% [coefficient of variation (C.V.)], and that the error due to sampling of this heterogeneous material is apparently much higher,[3] this < 0.03% value is negligible. Accordingly, there seems to be little need or desirability to expend time and effort to obtain complete dissolution for these sample types.

TABLE 2

PLUTONIUM IN RESIDUES FROM FUSION DISSOLUTION

Residue from Sample Type	Plutonium	
	mg.	% (sample basis)
Brick fines	0.0043	< 0.02
Crucible leach sludge	0.0015	< 0.03
Chemical waste	0.0520	< 0.01
Grinder sludge	0.0072	< 0.02

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FURTHER STUDIES ON THE ANION-EXCHANGE SEPARATION OF PLUTONIUM

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

At the New Brunswick Laboratory (NBL), plutonium is determined by constant-current potentiometry[1,2] after an anion-exchange separation of the plutonium from impurities.[3,4] In this separation, plutonium(IV) is added to the column in a 8N nitric acid solution, the impurities are eluted with 8N nitric acid, and finally the plutonium is eluted with 0.36M hydrochloric acid-0.01M hydrofluoric acid. In the present work, additional studies of this separation procedure were made. These studies involved (1) the conversion of plutonium to plutonium(IV); (2) the use of different batches of the customary resin, Bio-Rad AG-1, and a new resin, Bio-Rex 9.

EXPERIMENTAL

Reagents and Apparatus

Standard Plutonium Nitrate Solution, 0.03591 g. Pu/g. solution. This solution was prepared by dissolving plutonium metal in HCl and then evaporating three times with HNO_3 at about 60°C to minimize the formation of plutonium(VI). The final solution was made up to 8N HNO_3 and weighed. Weighed aliquots of this solution were analyzed to obtain the total plutonium by constant current potentiometry with the dichromate titrant standardized against National Bureau of Standards $Pu(SO_4)_2 \cdot 4H_2O$, NBS 944.

Standard Plutonium-Uranium Nitrate Solutions. Weighed aliquots of the standard plutonium nitrate solution were added to weighed quantities of a uranyl nitrate solution to give an approximate U to Pu ratio of 4 to 1.

Standard Plutonium Oxide Material, 87.06% Pu, a refractory (high-fired) oxide analyzed over a period of several months.

Standard (Plutonium-Uranium) Oxide. Weighed portions of the standard plutonium oxide were mixed with quantities of U_3O_8 to give a 4 to 1 ratio of U to Pu to simulate typical UO_2-PuO_2 samples.

Anion Resin, Bio-Rad Ag-1 (Dowex-1), nitrate-form, X-2 cross-linked, 100 to 200 mesh. (This resin is a strongly basic quaternary ammonium-polystyrene type.) The resin is stored in distilled water.

Anion Resin, Bio-Rex 9 (Permutit S-180), nitrate-form, 100 to 200 mesh. (This resin is a strongly basic pyridinium-polystyrene type.) The resin is stored in distilled water.

Ion-Exchange Resin Columns, 200-mm. long and 25-mm. ID, containing a glass-wool plug on the bottom. A column is filled to a settled bed-height of 50 mm. with a slurry of the resin. (For the samples fused with $NaHSO_4$ or containing more than 1 g. of sulfate, an 80-mm. bed-height is used.) The resin is washed with 100 ml. of 8N HNO_3 prior to use.

Procedure

Dissolve a weighed portion containing 200 to 300 mg. of plutonium by HNO_3-HF treatment or $NaHSO_4$ fusion according to standard methods.[5,6] Take up in 8N HNO_3 samples from the $NaHSO_4$ fusion as previously described,[6] and proceed directly with the resin slurry addition step below. Evaporate to incipient dryness nitrate solutions and solutions from the acid dissolution treatment in 250-ml. teflon beakers. Cool the beaker, rinse the beaker sides with 8N HNO_3, add 1 ml. of 30% H_2O_2, cover the beaker immediately and mix the solution by swirling. (The color of the solution at this step changes from red-brown, to emerald-green, finally to bright blue [Pu(III)]. In the presence of appreciable quantities of uranium, the final color may be yellow-green.) Allow the solution to stand for several hours or gently heat the solution until the color turns olive-green [Pu(IV)], or, in the presence of uranium, yellow olive-green.

Rinse the beaker sides and cover with 8N HNO_3, and add a thick slurry of resin in 8N HNO_3, sufficient to give a column settled-bed volume of about 20 ml. If the supernatant solution is colored when the resin settles, add additional slurry. In the case of uranium-plutonium solutions, add additional resin only until the supernatant is yellow.

Transfer the slurry to the column with 8N HNO_3. (The resin is difficult to wash out of a glass beaker, adhering tenaciously. From teflon, the quantitative transfer is much easier.) Adjust the flow rate to about 7 ml./min., and drain the solution to the resin bed. Place a plug of glass wool on the bed and wash the column with about 150 ml. of 8N HNO_3 if the solution contains 10 mg. or less of uranium. If more than this quantity of uranium is present, use the following quantities of 8N HNO_3:

U, mg.	8N HNO_3, ml.
up to 200	600
400	800
800	900
1300	1000

Elute the plutonium with 125 ml. of 0.36M HCl-0.01M HF solution, add 1 ml. of concentrated H_2SO_4 and evaporate to incipient dryness. Rinse down the beaker sides with 30 ml. of 1N H_2SO_4, add 1 ml. of concentrated H_2SO_4, and repeat the evaporation. Bring the solution up to about 20 ml. with 1N H_2SO_4 for the constant-current potentiometric determination of plutonium.

RESULTS AND DISCUSSION

Effect of Heating on Plutonium(IV) Oxidation State. The Pu(IV) oxidation state required for the ion-exchange separation[3] is obtained by treatment with hydrogen peroxide. The peroxide apparently converts the plutonium mostly to Pu(III) which is then oxidized to Pu(IV) on standing for several hours or by gently heating. Although the color change from blue to olive is quite distinct, in the presence of amounts of uranium greater than twice the plutonium, the color change from green to olive-yellow may be difficult to detect. In these cases, it is customary to ensure the complete conversion to the tetravalent state by heating the solution after the apparent color change for a short period of time. However, prolonged heating in 8N HNO_3 can cause oxidation to Pu(VI).[3,7]

Studies were made of the effect of heating plutonium and plutonium-uranium solutions at about 90°C for 30 min. after the apparent correct color change had occurred. The solutions were then carried through the ion-exchange procedure and titrated, Table 1. The data indicate that the heating period can be as long as 30 min. beyond the usual attainment of the Pu(IV) oxidation state. This heating step, therefore, is recommended as a precautionary measure to ensure the complete conversion.

TABLE 1

EFFECT OF HEATING SOLUTIONS AFTER COLOR CHANGE

Plutonium, mg. Added	Found		Recovery, %
198.18	198.34		100.08
204.93	205.05		100.06
201.81	201.93		100.06
196.35	196.33		99.99
		Average	100.04

Conversion of Pu(III) or Pu(VI) to Pu(IV) with H_2SO_4. The technique of fuming with H_2SO_4 was studied as an alternative to the usual peroxide treatment since in previous work[8] it was shown that this procedure can convert large amounts of Pu(III) and small amounts of Pu(VI) to Pu(IV).

In an initial study, three sets of plutonium and uranium-plutonium solutions were used. One set was fumed with H_2SO_4 three times to incipient dryness, the solutions were taken up in 8N HNO_3, separated by the column procedure, and titrated. Another set was separated without an oxidation state adjustment and then titrated. The last set was treated conventionally by peroxide, separated and titrated, Table 2. The data confirm that small amounts, about 0.2%, of Pu(VI) can be readily converted by the H_2SO_4 treatment.

TABLE 2

CONVERSION OF SMALL AMOUNTS OF Pu(VI) TO Pu(IV)

	Pu Recovery, %				
	Pu Solutions			U-Pu Solutions	
	No Treatment	H_2O_2	H_2SO_4	H_2O_2	H_2SO_4
	99.78	99.97	100.03	99.94	100.06
	99.83	99.97	100.03	100.00	100.00
		100.00	100.03	100.06	99.81
				100.00	99.99
					100.04
Average	99.80	99.98	100.03	100.00	99.98

In another series of tests designed to produce large amounts of Pu(VI), plutonium solutions were either heated under reflux for 72 hr. with 8N HNO_3 or evaporated to incipient dryness after each of two 8-hr. reflux periods. The solutions were then passed through the ion-exchange columns and titrated to determine the relative quantities of Pu(VI) and Pu(IV), Table 3.

TABLE 3

FORMATION OF Pu(VI) BY HNO_3 TREATMENT

	Treatment	
	Two 8-hr. Reflux Plus Evaporation to Dryness	72-hr. Reflux
Pu(IV) (retained), %	12.94	41.48
Pu(VI) (not retained), %	87.22	57.69
Total Pu, %	100.16	99.87

Plutonium solutions treated similarly were then fumed either three or six times with H_2SO_4 before being taken up in 8N HNO_3 for the ion-exchange separation and titration, Table 4. The data show that the large amounts of Pu(VI) obtained by the HNO_3 treatments cannot be converted to Pu(IV) by the H_2SO_4 fuming procedure.

TABLE 4

CONVERSION OF LARGE AMOUNTS OF Pu(VI) to Pu(IV)

Pu(IV) Recovery, %[a]	
Three H_2SO_4 Fumings	Six H_2SO_4 Fumings
89.43	91.90
75.02	94.72
84.37	93.66

a. Initial estimated sample composition: 20% Pu(IV), 80% Pu(VI).

Effect of Standing After Sodium Bisulfate Fusion and 8N HNO_3 Treatment on Pu(IV) Content. Previous work[6] has indicated that samples fused with $NaHSO_4$ and taken up in 8N HNO_3 can be separated quantitatively provided the resin column length is increased from 50 to 80 cm. The separation is normally carried out 24 hr. or less after the fusion. It is not known, however, if this waiting period can be extended.

To study the effect of a longer delay time in applying the separation, samples of PuO_2 and U_3O_8-PuO_2 (U:Pu ratio of 4:1) were carried through the fusion and separation procedure with and without a 5-day delay before the separation, Table 5. It is apparent that standing periods of 5-days can give recoveries low by 0.1 to 0.2%.

TABLE 5

EFFECT OF FIVE-DAY DELAY BETWEEN FUSION DISSOLUTION AND SEPARATION

	Pu Recovery, %			
	Normal Procedure (< 24 hr.)		5-Day Delay	
	PuO_2	U_3O_8-PuO_2	PuO_2	U_3O_8-PuO_2
	100.01	99.94	99.82	99.83
	99.97	100.05	99.99	99.80
	100.02	99.99	99.86	99.79
	99.98	99.95	99.80	99.79
Av.	100.00	99.98	99.87	99.80

Evaluation of Resins. Bio-Rex 9 resin has been reported to be more stable to radiation and HNO_3 than Bio-Rad AG-1 (Dowex-1).[9] The recovery of plutonium from plutonium nitrate solutions with this resin was tested. The results appear to be slightly high, averaging 100.06 in four runs. Some characteristics of the resin as compared to Bio-Rad AG-1 were observed: (1) it settles more rapidly in the column, (2) it does not adhere to glass surfaces as tenaciously; (3) it has faster sorption-elution times, (4) its darker color makes impossible any visual observation of the green plutonium band during separation.

Although Bio-Rad AG-1 has been used for many years at NBL and has given satisfactory recoveries of 99.99 $\pm$ 0.05%, in the past two years, differences have been noted between different batches of resin in recoveries and elution characteristics. These differences are shown in Table 6 along with the results shown by two different batches of Bio-Rex 9. Again, samples of NBS $Pu(SO_4)_2 \cdot 4H_2O$ No.944, plutonium solution and plutonium-uranium nitrate solutions were used in the tests. It is clear that the batches vary widely, and each batch received should be tested carefully to determine its acceptability.

TABLE 6

PLUTONIUM RECOVERY WITH DIFFERENT BATCHES OF RESIN

Bio-Rad AG-1							Bio-Rex 9	
A[a]	B	C[a,b]	D	E[a]	F	G[b]	A	B
98.88	99.99	99.80	99.84	100.01	99.95	99.62	99.91	100.05
98.79	99.97	99.77	99.92	100.01	99.99	99.52	99.94	100.04
98.82	100.06	99.76	99.87	100.05	100.04	99.47	99.86	100.04
	100.01	99.80		99.98	100.02	99.39		
Av. 98.83	100.01	99.78	99.88	100.02	100.00	99.50	99.90	100.04

a. diffuse sorption band, slow sorption-elution

b. large elution volume

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A CARRIER LAYER DISTILLATION METHOD FOR REFRACTORY MATERIAL IN URANIUM

H. G. Yuster and I. V. Nintzel

Direct spectrochemical methods of determining the refractory elements titanium, niobium, and zirconium in uranyl nitrate scrap and other uranium materials lack sensitivity. Preconcentration procedures involving chemical separations can provide adequate sensitivity, but the manipulations are time-consuming and tedious. Accordingly, the use of a carrier technique for these elements was investigated.

A thorough investigation of single carriers and combinations of two carriers was reported by Vogel.[1] An excellent review of the general use of carriers has been made by Pepper.[2] Silver chloride has been used with some success for determining refractories in uranium. In addition, it has been shown by various workers that the addition of fluorides to the silver chloride increases the sensitivity of response with adequate precision. This type of approach was used in the present work.

EXPERIMENTAL

Reagents and Apparatus

Silver Chloride, "Specpure," Johnson-Mathey, London, England.

Uranium Tetrafluoride, production-grade, Mallinckrodt Chemical Works.

Mixing Vials, polystyrene, 1/2 in. O.D. by 1 in. long, with 3/8 in. plexiglas ball, Spex Industries, Metuchen, New Jersey.

Spectrograph, Jarrel-Ash 3.4 m. Ebert, 15,000 lines/in. grating, 2.5 Å/mm. dispersion, set for 2900 to 3550 Å in second order, Jaco varisource.

Densitometer, Jarrel-Ash microphotometer.

Calculating Board, Applied Research Laboratories.

Procedure

Preparation of Standards. Dissolve 10 g. of high-purity U_3O_8 in HNO_3 and add the calculated quantities of titanium, niobium, and zirconium solutions to prepare a master standard. Add 2 ml. of H_2SO_4, evaporate to dryness and ignite the residue in platinum at 900°C for 2 hr. Transfer the cooled material to an agate mortar and finely grind, then ignite for an additional hour in platinum.

Finally, regrind and mix in the agate mortar. Prepare lower standards by dilution with the high-purity U_3O_8, Table 1. Prepare the carrier mixes as described below.

TABLE 1

LINE WAVELENGTHS AND CONCENTRATION RANGE OF STANDARDS

Element	Wavelength (Å)	Range of Standards (p.p.m.)
Nb	3358.42	10 - 0.5
Ti	3234.52	1 - 0.05
Zr	3391.98	10 - 0.5
U	3424.56	Internal Standard

Preparation of Electrode Charges. Convert samples to U_3O_8 by ignition, and pregrind in an agate mortar. Place 450 mg. of U_3O_8, 25 mg. of silver chloride and 25 mg. of uranium tetrafluoride in a mixing vial for the lower layer charge. Place 475 mg. of U_3O_8 and 25 mg. of silver chloride into a second mixing vial for the upper layer charge. Hand shake the vials for a few seconds and then shake for 1 min. in a Wig-L-Bug. Prepare the charges of the standards similarly.

Exposure Conditions

Excitation:	14 amp. (shorted), 220 VDC
Electrodes:	Upper, ASTM C-1 Lower, NCC SP9066
Electrode Gap:	4 mm.
Electrode Charge:	50 mg. of "lower mix" tamped, plus 50 mg. of "upper mix", vented with standard punch
Slit Dimensions:	14 microns wide, 9.1 mm. high
Sector:	Seven step rotating
Step Ratio:	$I_0/I = 2$
Photographic Plate:	4- x 10-in. Eastman Kodak Spectrum Analysis No. 1
Plate Processing:	D-19, 3 min. Short stop, 30 sec. Kodak Rapid Fixer, 2 min. Wash, 2 min.

Calculations

Densitometer the zirconium line because of the excessive background (plus weak unresolved uranium line). Correct the zirconium line transmission for background on the low wavelength side. Use the uranium line listed in Table 1 as the internal standard to obtain log I_{Zr}/log I_U values. Estimate the titanium and niobium visually to the limits of detection listed in Table 2.

TABLE 2

LOWER LIMITS OF SENSITIVITY WITH VARIOUS MIXED CARRIERS

Element	AgCl-SrF_2[3]	AgCl-AgF[4]	AgCl-LiF[5,6]	AgCl-UF_4
Nb	---	4	6, 1	1
Ti	5	4	4, 0.3	0.5
Zr	10	10	20, 10	1

RESULTS AND DISCUSSION

Initial attempts to obtain a desirable carrier burn involved the use of a 3-mil teflon disk placed beneath a U_3O_8-silver chloride charge in a regular carrier electrode. This procedure showed some promise in that the refractory elements were excited satisfactorily; however, the decomposition of the teflon was extremely rapid even at reduced amperage. Uranium was also excited excessively and a complex spectra with heavy background was obtained. In later tests with the carrier layer technique, indium fluoride, gallium fluoride, copper fluoride, and finally uranium tetrafluoride was used in the bottom layer of the charge. Uranium tetrafluoride was selected as the best fluoride compound for two reasons: (1) it duplicated the matrix material and therefore did not introduce additional spectra; (2) it gave essentially the best sensitivity, at least for zirconium.

With the top layer consisting of 95% U_3O_8-5% silver chloride and the bottom layer of 90% U_3O_8-5% silver chloride-5% uranium tetrafluoride, the limits of sensivity shown in Table 2 were obtained. Visual estimates were used for the titanium and niobium. Comparisons with other mixed carrier methods are also shown in this table. While this report was being prepared, a mixed fluoride carrier procedure[6] was described that showed nearly the same sensitivity as the proposed method for titanium and niobium. The sensitivity for zirconium is apparently better in the proposed method. The standard curve for zirconium is shown in Figure 1.

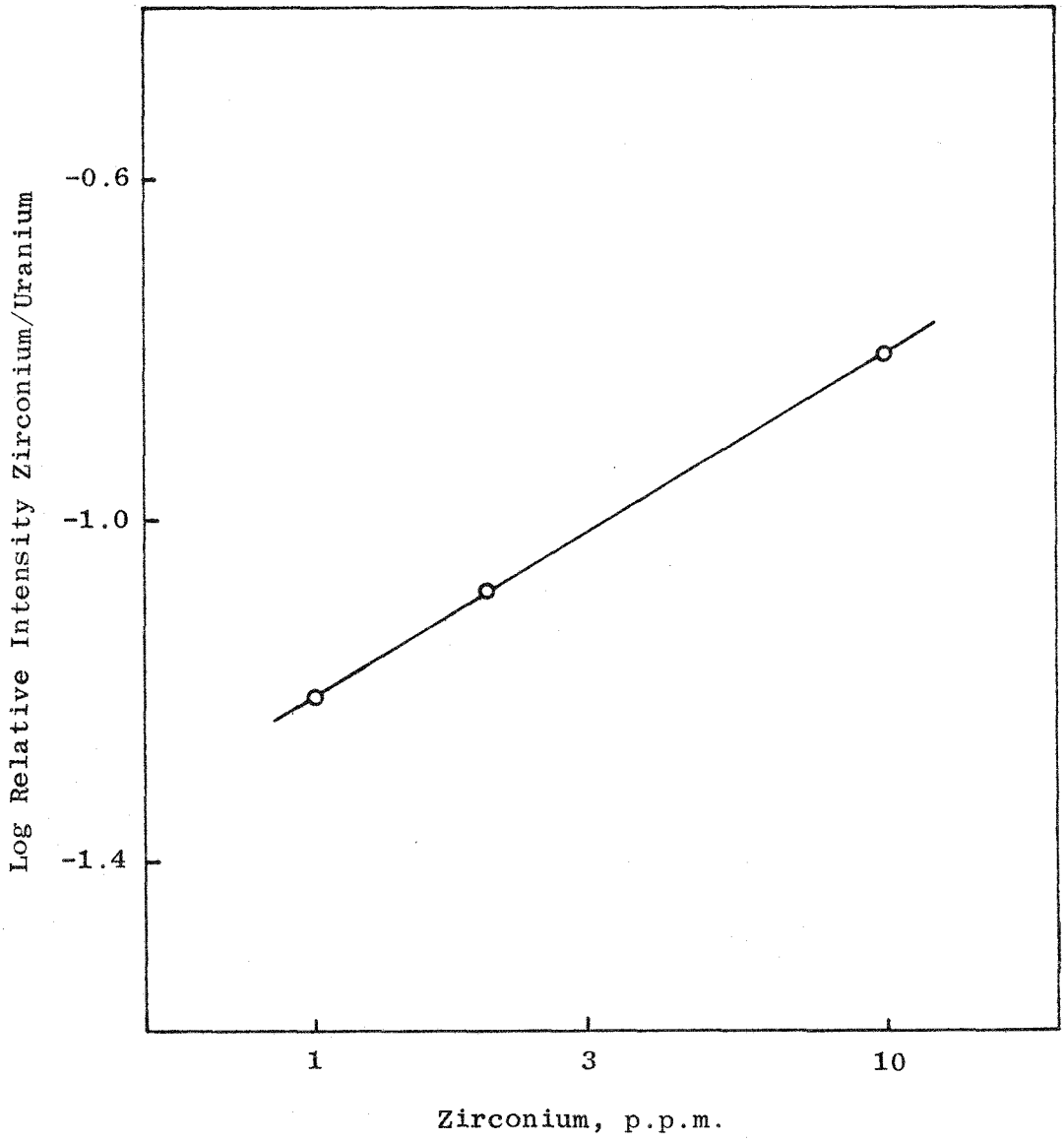

FIGURE 1. ANALYTICAL CURVE FOR ZIRCONIUM IN U_3O_8

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COMPARISON OF ATOMIC ABSORPTION AND EMISSION SPECTROMETRIC DETERMINATION OF IMPURITIES IN URANYL NITRATE

H. G. Yuster and R. L. Graff

The determination of impurities in samples of uranyl nitrate crystals is one phase of the enriched uranium scrap recovery General Analytical Evaluation Program (GAE).[1] In this evaluation program, one reference sample and one production sample are analyzed each month by various laboratories. For a 6-month period, the reference samples are identical and the monthly production samples are different samples. Most laboratories involved in the program use emission spectroscopy to determine the impurities. At the New Brunswick Laboratory (NBL), six elements have been determined both by atomic absorption and emission spectrometry for some time. This report presents a brief comparison of the results obtained by these two methods.

EXPERIMENTAL

Instruments

Atomic Absorption Spectrometer, Perkin-Elmer No. 403, with associated high-intensity hollow cathode lamps.

Emission Spectrograph, Jarrel-Ash 3.4 m. Ebert, 15,000 lines/in. grating, 5 Å/mm. dispersion, Jaco Varisource.

Procedures

For the atomic absorption spectrophotometric determinations prepare final solutions of the uranyl nitrate crystals to contain 2% uranium and 5% by volume of distilled HNO_3. To obtain the required uranium content, assume the crystals to contain 52% uranium. Prepare standards similarly from pure U_3O_8, known to contain only insignificant amounts of the 6 elements concerned, by adding the elements in the desired concentration. Use the air-acetylene flame for the chromium, copper, iron, manganese, and nickel measurements, and the nitrous oxide-acetylene flame for the aluminum.

For the emission spectrographic determinations, convert 4 g. of the crystals to U_3O_8 by heating the material in a platinum dish under an infrared lamp until gas evolution ceases, then igniting in a muffle furnace at 900°C for 2 hr. Grind the oxide in an agate mortar. Analyze the U_3O_8 by the gallium oxide carrier distillation procedure already described[2] for all the elements except aluminum. Determine aluminum by the silver chloride-uranium tetrafluoride carrier technique.[3] Use standards similar to those described in this same report[3] for the aluminum calibration curve; for the curves of the other elements, use NBL U_3O_8 emission spectrographic standards series 95.

RESULTS AND DISCUSSION

The results for two six-month periods are shown in Table 1 (reference sample) and Table 2 (production samples). The complete data for all impurity elements can be found in reference 4. Precision studies made on the reference samples are shown in Table 3.

From the data shown in Tables 1 and 2 it can be seen that, aside from an occasional anomalous result, the agreement between the individual results of the two methods is generally good. Disagreement appears most often in the aluminum, chromium, and nickel values of the production samples. The reason for the occasional disagreement is being studied further, but a handicap to the study is the lack of sufficient quantity of the production samples; synthetic solutions must be relied upon. The average values in Tables 1 and 2 agree remarkably well in most cases; therefore, one method does not show a significant bias as compared to the other.

The data in Table 3 indicate that the average precisions for the two methods are identical although the individual values do vary somewhat. Table 3 also shows improved precisions of both methods for the second 6-month period. Except for the possibility of a more homogeneous sample for this second period, this improved precision cannot be explained. One change made in the second period was the conversion of a larger sample, about 6 g., of crystals to U_3O_8 and the use of this material for both methods. However, it is difficult to understand how this modification could have improved the precision of the emission spectrography.

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TABLE 1

REFERENCE SAMPLE RESULTS IN P.P.M. FOR TWO 6-MONTH PERIODS

Period	Al		Cr		Cu		Fe		Mn		Ni	
	E.S.*	A.A.**	E.S.	A.A.	E.S.	A.A.	E.S.	A.A.	E.S.	A.A.	E.S.	A.A.
Jan.-June 1969	6	7	8	9	2	1	25	25	4	2	8	2
	8	12	14	6	2	1	33	26	1	1	13	11
	6	10	7	5	7	3	28	34	1	1	6	4
	7	7	5	5	1	1	28	29	1	2	14	13
	7	3	5	5	2	2	29	33	2	1	10	11
	6	8	4	6	2	2	27	27	1	2	6	12
Average	6.7	7.8	7.2	6.0	2.7	1.7	28	29	1.7	1.5	9.5	8.7
March-Aug. 1970	6	4	23	20	1.6	1.6	80	81	5	3	16	15
	5	4	15	22	2	3	81	91	3	3	16	13
	4	4	12	20	2	2	85	102	2	4	15	12
	5	4	15	20	2	3	90	92	3	3	16	11
	5	7	17	23	3	2	95	95	3	3	17	15
	6	7	18	24	2	2	90	103	3	3	19	15
Average	5.2	5.7	17	22	2.1	2.3	87	94	3.2	3.2	17	14

* Emission Spectrographic

** Atomic Absorption

TABLE 2

PRODUCTION SAMPLE RESULTS IN P.P.M. FOR TWO 6-MONTH PERIODS

Period	Al		Cr		Cu		Fe		Mn		Ni	
	E.S.*	A.A.**	E.S.	A.A.	E.S.	A.A.	E.S.	A.A.	E.S.	A.A.	E.S.	A.A.
Jan.-June 1969	20	45	20	11	1.3	2.5	55	34	5	2	15	3
	25	15	26	31	3	2	135	146	6	5	28	34
	20	25	110	95	5	5	510	480	19	12	100	60
	20	35	20	17	7	5	110	105	3	4	24	23
	20	15	35	43	6	4	180	190	6	5	48	43
	22	20	12	12	8	7	65	56	3	3	15	18
Average	22	26	37	35	5	4.3	176	169	7	5	38	30
March-Aug. 1970	21	28	13	14	1.1	0.8	38	49	3	2	10	12
	2	6	4	6	1	2	21	22	2	2	7	8
	5	4	6	10	2	2	45	59	1	2	9	8
	40	34	10	14	3	4	60	69	2	2	18	16
	180	320	19	30	2	2	118	115	3	3	18	17
	23	25	20	18	5	4	110	122	4	3	12	16
Average	45	70	12	15	2.6	2.5	65	73	2.5	2.3	12	13

* Emission Spectrographic ** Atomic Absorption

TABLE 3

PRECISION DATA FOR REFERENCE SAMPLES

Period	Element	Emission Spectrographic C.V.* %	Atomic Absorption C.V., %
Jan.-June 1969	Al	12	26
	Cr	51	26
	Cu	78	100
	Fe	10	13
	Mn	64	33
	Ni	36	53
	Average	42	Average 42
March-August 1970	Al	14	30
	Cr	22	8
	Cu	24	26
	Fe	6	9
	Mn	31	19
	Ni	8	13
	Average	18	Average 18

* Coefficient of Variation

SIMULTANEOUS DETERMINATION OF CARBON AND SULFUR IN URANIUM DIOXIDE AND BORON

Ted D. Tarr

A commonly-applied method for the determination of carbon in non-ferrous metals involves high-frequency induction heating and a gas chromatographic measurement. As a result of a previous study,[1] this method is being relied upon at New Brunswick Laboratory (NBL) for routine carbon analyses of uranium, uranium dioxide, black oxide, thorium, boron, and boron carbide.

Recently, both carbon and sulfur measurements have been required for certain samples. Sulfur combines with oxygen to form sulfur dioxide which is readily measurable by gas-solid chromatography. It seemed possible that this feature could be incorporated into the carbon analysis to give a fast and accurate method for the determination of both elements.

EXPERIMENTAL

Apparatus

Induction Furnace, Leco Model 523 high-frequency induction furnace with a quartz combustion tube.

Gas Chromatograph. A Varian Aerograph 1520 gas chromatograph equipped with dual thermal conductivity detectors and using helium as the carrier gas is coupled to the induction furnace. Dummy 1' x 1/8" copper columns are used in the chromatograph. The detectors are operated at a current of 200 ma. and a block temperature of 205°C. The column oven and injector ports are operated at 170°C. The helium pressure is 50 p.s.i.g. at the column head.

Collection Column or Loop. A 1' x 1/4" stainless steel column, packed with 50/80 mesh Porapak Q-S, is bent into a U-shape and connected to two four-port switching valves. The column is conditioned at 220°C for 12 hr. with helium passing through it.

Crucibles and Accelerator. Leco combustion crucibles are baked out overnight at 1100°C before being used. The accelerator charge consists of 1.90 g. granular analytical-grade copper, 0.80 g. Leco low-carbon iron chips, and 0.40 g. Leco granular tin mixed in the crucibles.

Recorder, a Brown 1-mv. recorder equipped with a disc integrator.

Procedure

Remove a crucible from the furnace and allow it to cool before

loading with the accelerator and sample mixture. Place the crucible in the combustion tube. Set the oxygen flow at 2.0 l./min. Burn for 5 min. and sweep the tube for 2 min. more. Collect the gases in the loop which is cooled to -78°C with a dry ice-ethanol slurry. Sweep the loop with helium for 1 min. to remove all the oxygen. Switch the loop completely into the carrier gas stream and allow the flow to stabilize for 3 min. Heat the loop with room-temperature water to release the carbon dioxide. (This peak will appear about 30 sec. after the application of the water.) Immediately after the carbon dioxide peak has been measured, apply the external heat source, heated to 170°C, to the loop in order to elute the sulfur dioxide. (The sulfur dioxide peak will appear in about 6 min.)

Obtain calibration curves by burning known amounts of NBS steel standards and plotting peak area as obtained by the disc integrator versus quantity of carbon or sulfur. (Linear curves are obtained in the 5- to 30-μg. range for both elements.)

RESULTS AND DISCUSSION

Uranium dioxide and elemental boron samples were analyzed with and without the addition of sulfur, Table 1. Approximately 95% of the sulfur was recovered from both the boron and uranium dioxide samples.

TABLE 1

ANALYSIS OF SAMPLES WITH AND WITHOUT ADDED SULFUR

Sample	Carbon, p.p.m.	Sulfur, p.p.m. Added	Sulfur, p.p.m. Found
UO_2	5.7	0	3.4
	5.7	0	3.1
	4.5	0	2.0
	6.5	0	2.2
	5.7	0	3.1
	4.8	0	3.0
		120	114
		120	120
Boron NBL F-5867	410	0	0
	398	1000	960
F-5868	843	0	0
	819	1000	930

Attempts to determine sulfur in silicone elastomer and boron-filled silicone elastomer were unsuccessful. Apparently some unidentified organic product prevented either the formation or collection of the sulfur dioxide.

REFERENCE

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TENTATIVE METHOD FOR THE ASSAY OF BORON TRIFLUORIDE-DIMETHYL ETHER

A. R. Eberle and M. W. Lerner

Existing methods for the determination of boron in boron trifluoride organic coordination compounds are summarized by Booth and Martin.[1] They are based either on the formation and weighing of an insoluble addition compound as shown in reaction 1,

$$(CH_3)_2O \cdot BF_3 + NaF \rightarrow (CH_3)_2O + \underline{NaF \cdot BF_3} \qquad 1$$

or on the precipitation and filtration of an insoluble fluoride as in reaction 2 followed by a conventional mannitol titration of the resulting boric acid.

$$2\,(CH_3)_2O \cdot BF_3 + 3\ CaCl_2 + 6\ H_2O \rightarrow 2\,(CH)_2O + 3\ CaF_2 + 6\,HCl + 2\,H_3BO_3 \qquad 2$$

The accuracy of methods involving the weighing of an addition compound is said to be within 0.5%, with the results being generally high due to the non-volatile impurities. The second method is stated to be more precise but it is time-consuming and requires careful addition of the calcium salt to avoid formation of calcium fluoroborate. Moreover, the calcium fluoride may be difficult to filter.

Since thorium is one of a group of few elements that do not form fluoroborates,[1] and is the only element in this group that forms an insoluble fluoride, it seemed likely that a better example of the general method involving the precipitation of an insoluble fluoride to liberate boric acid would be as follows:

$$4\,(CH_3)_2O \cdot BF_3 + 3\ Th(NO_3)_4 \cdot 4H_2O + 8H_2O \rightarrow 4\,(CH_3)_2O$$

$$3\ ThF_4 + 12\ HNO_3 + 4\ H_3BO_3 \qquad 3$$

Moreover, thorium nitrate is fairly soluble in methyl alcohol. It was found in previous work[2] that the boron in methyl alcohol solution essentially free of water can be recovered completely by distillation in the first half of the distillate. This type of methyl borate distillation is much more efficient than the distillation of boron in methyl alcohol-aqueous solutions in which multiple distillations are required to recover the boron completely. Accordingly, the thorium nitrate can be dissolved in methyl alcohol, the etherate added, and the mixture only partially distilled to obtain complete recovery of the methyl borate. It would remain, then, simply to distill off the methyl alcohol and some residual ether from the distillate solution made alkaline, and then to titrate the boric acid in the usual way. Some experiments using this method were carried out in the present work.

EXPERIMENTAL

Reagents and Apparatus

Methyl Alcohol, 99%.

Thorium Nitrate Tetrahydrate

Mannitol

Sodium Hydroxide, 0.4N, standardized against standard boric acid and stored in polyethylene.

Distilling Flask, quartz, 500-ml., with quartz condenser fitted with a 6-in. length of 1/4-in. I.D. gum rubber tubing at the outlet end.

Platinum Dish, 500 ml.

pH Meter.

Procedure

Add to the distilling flask 8 g. of thorium nitrate and 150 ml. of methyl alcohol. Stir with a magnetic stirring bar until the salt is dissolved. Place a glass funnel in the flask with the tip immersed in the solution. Add, from a weight buret with the tip at the vortex of the funnel, 1.3 to 1.4 g. of the etherate, and quickly wash down the funnel with 50 ml. of methyl alcohol. Connect the condenser and immerse the rubber outlet tip in 100 ml. of water in the platinum dish. Add 6 pellets of sodium hydroxide and 1 drop of 1% phenolphthalein solution to the water.

Immerse the distilling flask in a water bath held on a magnetic stirrer-hot plate and stir for 5 min., then heat the water bath to 76 to 78°C and distill off 125 to 135 ml. of methyl alcohol. Avoid "suck-back", which may occur when the fast evolution of the ether slows down, by momentarily lifting the rubber tip out of the solution.

Place the distillate on a steam bath and evaporate to dryness. Dissolve the residue in 100 ml. of water and transfer the solution to a 400-ml. beaker. Add dilute H_2SO_4 to pH 2, boil momentarily with the beaker covered to remove carbon dioxide, and cool to 25°C in a cold water bath. Titrate the boric acid in the usual way, using 30 g. of mannitol after the strong acid endpoint and determining the endpoints from the second derivative of the potentials.

RESULTS AND DISCUSSION

The efficiency of the distillation recovery of the methyl borate was tested by dissolving a weighed portion of the etherate in 200 ml. of methyl alcohol containing 8 g. of thorium nitrate and distilling off the alcohol in 50-ml. portions. Analysis of these portions indicated that 99.9% of the ester was distilled off

in the first 100-ml. Therefore, a distillate of 125 to 135 ml. was deemed sufficient for complete recovery.

The use of calcium instead of thorium to tie up the fluoride was tested. With 5 g. of anhydrous calcium chloride used in place of the thorium nitrate the recovery was 91.0% in 135 ml. of distillate.

Reaction 3 indicates that 8 moles of water are required for every 4 moles of etherate. In the exploratory tests with the thorium, no water other than that in the thorium nitrate was added. Apparently there is sufficient water in the methyl alcohol to satisfy the reaction requirements.

Table 1 gives the results of a series of determinations on a production sample of boron trifluoride-dimethyl methyl ether. The actual purity of the sample is unknown; for 100% purity, the theoretical boron value is 8.93% for an atomic weight of 10.1084. Most of the results are somewhat below this theoretical value. There are two factors in the present procedure that can contribute to low results. Some loss of boron can undoubtedly occur in the weighing of the etherate and transfer operation: the etherate is extremely volatile and hydrolyzes readily with atmospheric moisture. Another potential source of negative errors is the distillation step in which the first portion of gas is rich in dimethyl ether which bubbles vigorously through the dilute sodium hydroxide solution trap. Some methyl borate may not be trapped in this initial surge of gas. Two changes in the procedure may be helpful to prevent these errors. The weighing and transfer step can be carried out in a dry box. A more efficient means of trapping the methyl borate in the distillation, perhaps in the form of a column, would also be helpful.

TABLE 1

ANALYSIS OF A BORON TRIFLUORIDE-DIMETHYL ETHER SAMPLE

(Theory = 8.93% B)

Number of Determinations	Boron Found, %	Coefficient of Variation, %
16	8.89	0.43

REFERENCES

1. Booth, H. S. and Martin, D. R., "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York (1949).

2. Eberle, A. R. and Lerner, M. W., Anal. Chem., 32, 146 (1960).

DETERMINATION OF FLUORIDE IN BORON BY PYROHYDROLYSIS AND A FLUORIDE-SPECIFIC ELECTRODE MEASUREMENT

Ted D. Tarr

Pyrohydrolysis, generally accepted as an excellent technique for the separation of fluoride from a variety of materials and described in detail by Powell and Menis,[1] has been used at the New Brunswick Laboratory (NBL) to separate the fluoride from elemental boron. The separated fluoride is determined by a spectrophotometric procedure involving the bleaching of the thorium-alizarin red S complex color.[2] Although recovery of the fluoride in the pyrohydrolysis step of this procedure is essentially complete, occasionally low recoveries are obtained. In the present work, steps were taken to improve the recovery of the fluoride by means of a different pyrohydrolysis accelerator.

Recent developments[3] in the field of ion-specific electrodes have stimulated the use of the fluoride-specific electrode for the determination of fluoride. This type of determination was used in the present work.

EXPERIMENTAL

Reagents and Apparatus

Sodium Tungstate-Tungstic Trioxide Flux, prepared by the following procedure.[4] Sodium tungstate, 165 g., is heated gently in a platinum dish over a Meker burner to dehydrate the salt. The salt is transferred to a porcelain mortar, 116 g. of tungstic oxide is added, and the mixture is ground intimately. The mixture is transferred to the platinum dish and is heated gradually over the Meker burner to a dull red heat, this heat being maintained for 2 hr. The melt is cooled, the cake is dislodged and is ground, a portion at a time, in a clean mortar to a coarse powder. The powder is stored in an air-tight bottle.

Sodium Hydroxide, 0.05N.

Buffer Solution, pH 5, prepared by mixing 0.1N sodium acetate and 0.1N acetic acid.

Stock Standard Fluoride Solution, 1.0 mg./ml. Solutions of 50 and 5 μg./ml. are prepared by dilution of the stock solution. All standard solutions including the stock solution are prepared fresh at least every two weeks.

Pyrohydrolysis Unit, consisting of a quartz delivery tube fitted with perforated teflon tip, tube furnace and thermocouple, oxygen flow-meter, 25-ml. centrifuge tube receiver, gas-washing bottle fitted with a coarse glass frit, and quartz combustion boats.

Fluoride-Specific Electrode, Orion Research, Inc.

pH Meter, expanded scale.

Procedure

Mix intimately by grinding in a mortar 8 g. of the sodium tungstate flux and 200 mg. of sample. Transfer the mixture to a quartz boat and insert the boat into the pyrohydrolysis tube. Pyrohydrolyze at 1000°C with oxygen, passed initially through the column of water in the gas-washing bottle held in a water bath near 100°C, being swept through at 2.0 l./min. Immerse the outlet tip to the bottom of the 25-ml. centrifuge tube containing 15 ml. of the 0.05N sodium hydroxide solution. Pyrohydrolyze for 15 min. Remove the centrifuge tube and rinse down the tip with water.

Transfer the solution to a 100-ml. plastic volumetric flask. Add 50 ml. of buffer solution, bring up to volume with water, and transfer the solution to a plastic beaker. Begin magnetic stirring and insert the fluoride-specific and calomel electrodes. Record the equilibrium potential.

Prepare a standard curve by adding from 5 to 100 μg. of fluoride to plastic 100-ml. volumetric flasks, adding to each flask 50 ml. of buffer, 15 ml. of 0.05N sodium hydroxide solution and sufficient water to bring the solution to the mark, and obtaining the equilibrium potentials. Plot the potential vs. fluoride concentration on semi-log paper with the potential on the linear ordinate.

RESULTS AND DISCUSSION

In previous work,[5] the fluoride-specific electrode was found to be most effective when used in a buffered medium at pH 5. At this pH, at least 200 mg. of boric acid, small quantities (< 50 mg.) of which are usually distilled along with the fluoride, was found to have no effect on the fluoride potential.

The existing NBL method[2] for determining fluoride by pyrohydrolysis involves the use of a U_3O_8 bedding and accelerator material. Recovery of the fluoride is generally complete only after 90 min. of pyrohydrolysis at 1000°C. In a recently published procedure,[4] the use of an acidic oxide accelerator-low melting flux mixture as represented by tungsten oxide-sodium tungstate was recommended. Powell and Menis[1] also used tungstic oxide as an accelerator. Accordingly, the tungstic oxide-sodium tungstate mixture was studied by analyzing samples of an ultra-high purity boron (Eagle-Picher hot-wire material), known to be essentially free of fluoride, with and without added fluoride, Table 1.

TABLE 1

RECOVERY OF FLUORIDE FROM 200-mg. BORON

Pyrohydrolysis Time, min.	Oxygen Flow Rate, l./min.	Fluoride, μg. Added	Fluoride, μg. Found
15	2.0	0	0
15	2.0	0	0
5	2.0	100	65
5	2.0	100	85
5	2.0	200	170
10	2.0	100	98
15	1.0	100	60
15	1.0	200	135
15	2.0	100	100
15	2.0	200	195
15	2.0	200	202

It can be seen that the accelerator is very effective. Complete recovery of the fluoride is obtained in 10 to 15 min. at 1000°C with a flow rate of moist oxygen of 2.0 l./min. This fast flow rate is necessary; with a flow rate of 1.0 l./min., a white fog appears in the exit gas and the recovery is low in the 15-min. pyrohydrolysis time.

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1. Powell, R. H. and Menis, O., Anal. Chem., 30, 1546 (1958).

2. Goldbeck, C. G. and Lerner, M. W., NBL-242 (March 1968), p.4.

3. Raby, B. A. and Sunderland, W. E., Anal. Chem., 39, 1304 (1967).

4. American Standards Association, "Referee Methods for the Chemical Analysis of Nuclear Fuels," ASA N5.7-1965, p. 37.

5. Goldbeck, C. G. and Nepote, K. H., unpublished data, 1968.

SAFEGUARDS ANALYTICAL LABORATORY EVALUATION (SALE) PROGRAM

M. W. Lerner and C. E. Hedrick

The USAEC Office of Safeguards and Material Management is sponsoring a Safeguards Analytical Laboratory Evaluation program which is being conducted by the New Brunswick Laboratory (NBL). This program is an integral part of the AEC's efforts to continually upgrade safeguards against the unlawful diversion of special nuclear material, and is particularly important to the accountability aspects of the Safeguards program.

The SALE program is designed to measure the precision and accuracy associated with the routine chemical analyses and isotopic determinations performed by laboratories involved in processing nuclear materials and by any other interested laboratory. The results of this program will improve the ability of the AEC to evaluate the flow and inventory data of special nuclear material.

The first material to be considered in the SALE program is uranium dioxide. Samples of uranium dioxide are being distributed to 34 domestic laboratories and 3 foreign laboratories. In general, each laboratory receives one sample a month for 6 months. At the present time all of the samples have been distributed and many results have been received by NBL. As soon as the compilation is complete, the data will be analyzed statistically and a report issued.

Other materials that are being considered for distribution in the future as a part of the SALE program are plutonium metal, plutonium oxide, plutonium dioxide-uranium dioxide, and plutonium nitrate.

A COMPUTER-CONTROLLED MASS SPECTROMETER DATA ACQUISITION LABORATORY

L. C. Nelson, Jr.

A computer-controlled isotope-ratio mass spectrometer system, described in a previous report,[1] has been in satisfactory operation for about ten months. The system now has been expanded to include two additional mass spectrometers. Two of the three instruments are used for uranium analysis and one for boron. They are used on a "queue-up" basis by the individual operators.

A pulse-height analyzer system is being developed to utilize the spare capacity of the computer.

Equipment

All of the peripheral equipment interfaced to the PDP-8 computer is shown in Figure 1. The PDP-8 unit has a 4K memory and the disk file has a 32K storage capacity. The analog-to-digital converter has a 12-bit capacity and a 16-channel multiplexed input. Signal range is 0 to 10 volts.

The relay buffer driver is a 32-channel unit which controls a series of dry reed relays mounted on plug-in circuit boards[1] located in the vibrating reed electrometer (VRE) and magnet control panels of each spectrometer. The remote teleprinter is located in the mass spectrometer laboratory and the local teleprinter is located at the computer console in a room across the hall. A schematic diagram of a relay switch used to activate the proper mass spectrometer as chosen by an operator is shown in Figure 2. The switch is located between the relay buffer driver and the mass spectrometers. The relays are the same as used in the VRE's and magnet control panels, and are used to route the -15 volt signal to the instrument selected.

The pulse-height analyzer/scope display interface and the high speed reader/punch shown in Figure 1 are not used in the mass spectrometer system.

System Description. Figure 3 is a core map of the system operating program which is permanently stored and protected as a system program on the disk storage unit. The program uses 22 of the 32 pages of core memory. The disk monitor is permanently located on the top page of memory and provides the logic to call the operating program or any other program stored on the disk. A copy of the program is also punched on mylar tape as a back-up in the event of a disk system failure.

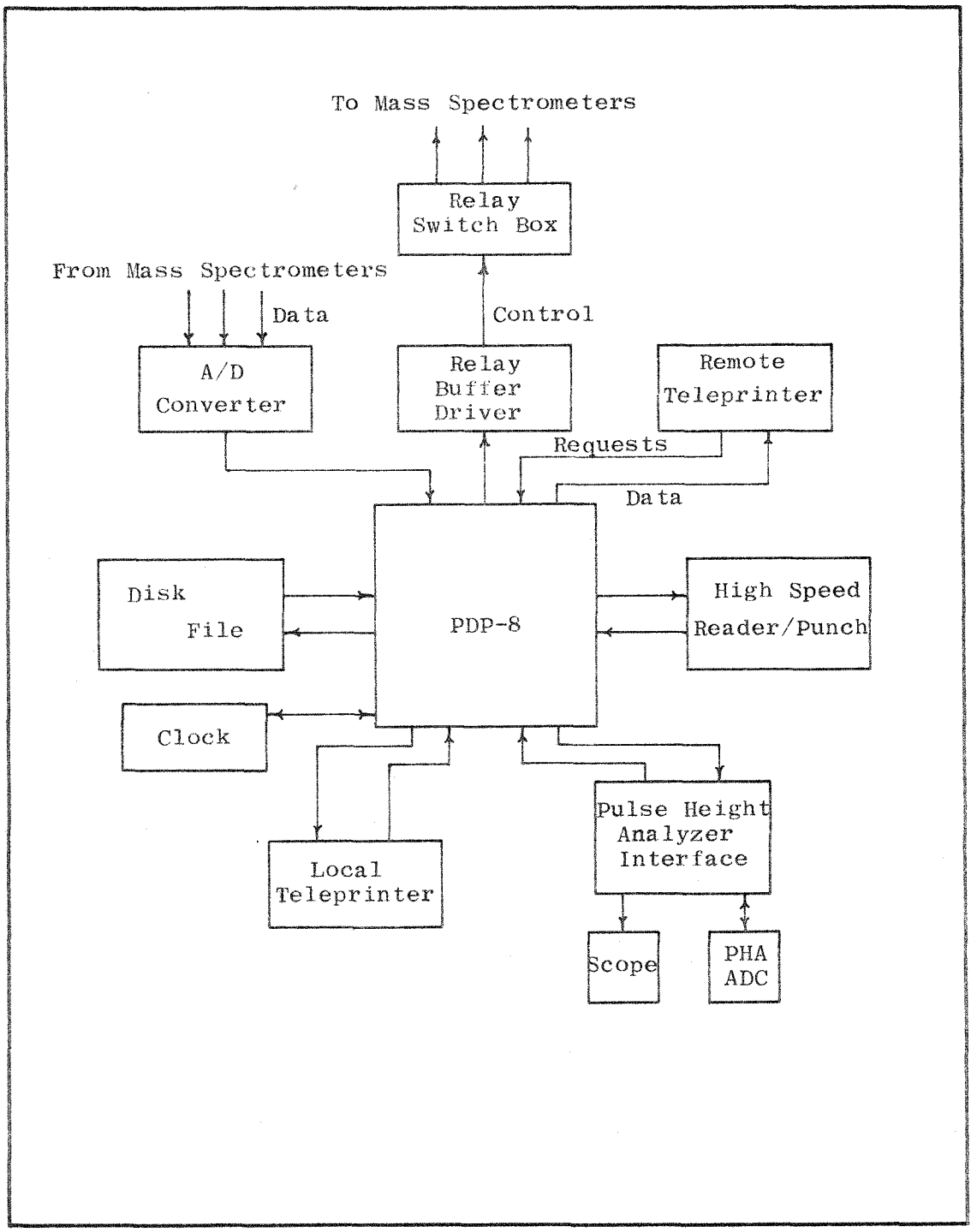

FIGURE 1. BLOCK DIAGRAM OF COMPUTER OPERATING SYSTEM SHOWING ALL PERIPHERALS.

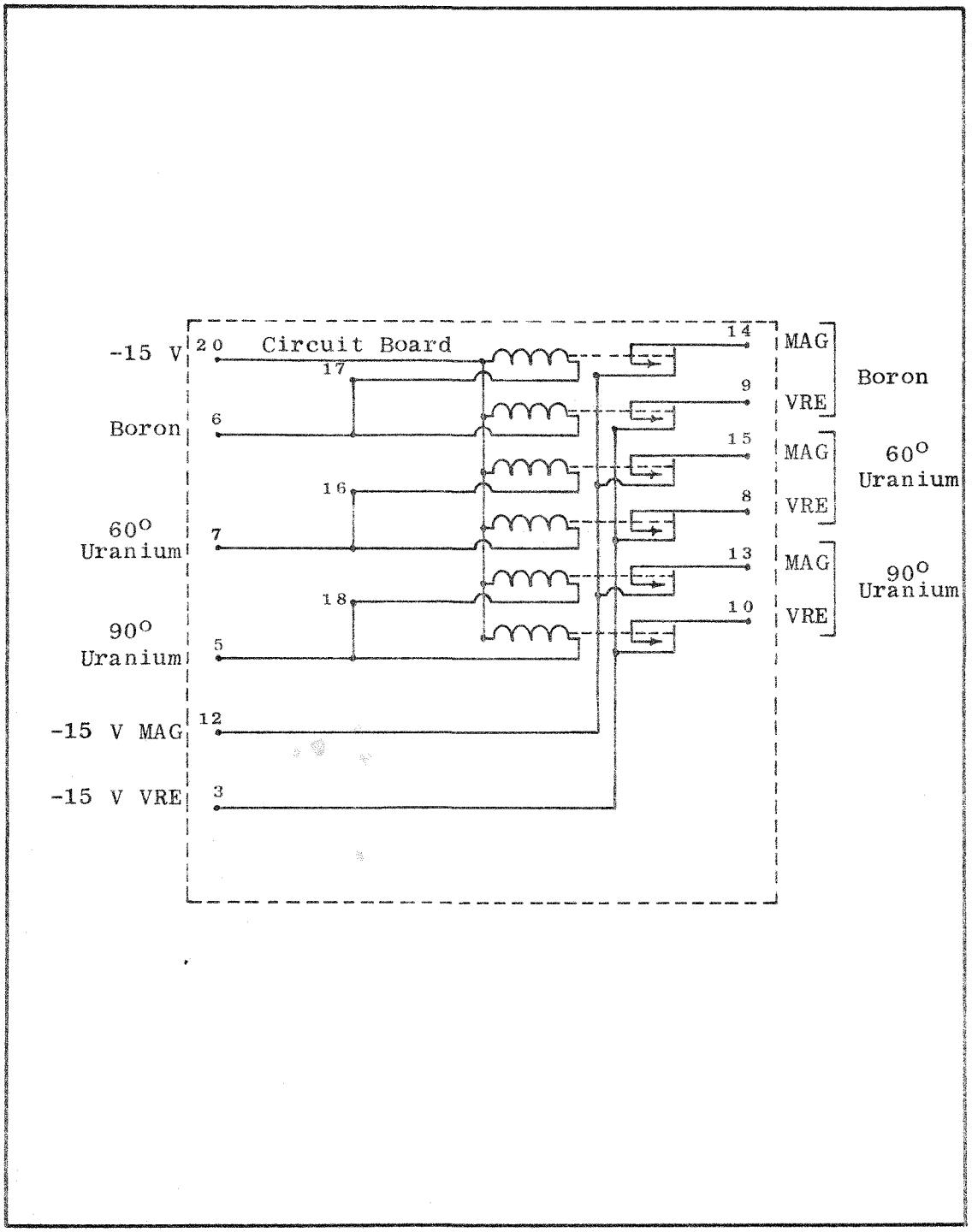

FIGURE 2. RELAY SWITCH BOX USED TO SELECT PROPER INSTRUMENT FOR OPERATION.

OPERATING PROGRAM CORE IMAGE

LOCATION	DESCRIPTION	REMARKS
0	DATA STORAGE, REFERENCES AND LINKS	
200	INTERRUPT SERVICE	
400	MESSAGE SERVICE	
600	MAIN OPERATING PROGRAMS	CALLED FROM DISK
1000	STD DEVIATION SERVICE	
1200	" " "	
1400	DATA CLEAR AND PROGRAM START	
1600	ALPHANUMBERIC STORAGE	
2000	DATA ACQUISITION	
2200	FINAL CALCULATIONS	CORRECTION FACTORS
2400	DATA OUTPUT	
2600	REMOTE KEYBOARD SERVICE	
3000		
TO	AVAILABLE FOR PHA DATA	FOUR PAGE DEBUGGING PROGRAM RUNS HERE.
5000		
5200	LOCAL KEYBOARD SERVICE	
5400		
TO	FLOATING POINT PROGRAM	
7400		
7600	SYSTEM MONITOR HEAD	

FIGURE 3. MASS SPECTROMETER OPERATING CORE MAP

One of the three main operating pages is called from the disk when a request from a mass spectrometer operator is made on the remote teleprinter. These main operating programs contain certain variations depending on the mass spectrometer being used. The clear and set-up page types queries to allow the recording of the sample number and to determine the number of peaks to be measured. The data acquisition page provides for setting the magnet, for adjusting the VRE, for collecting the data, and for performing preliminary calculations such as the subtraction of background, the determination of cumulative ratios, and the temporary data storage on page zero. Ratios and standard deviations are output at the completion of each set of peaks by means of the standard deviation subroutine. The calculation page performs the final calculations using the floating point program after suitable corrections are typed in by the operators. Final data are provided by the output page and the identifying wording is obtained from the alphanumerics page.

The interrupt page has the function of sorting the various requests for service from all input/output devices and of saving the active registers and program counter whenever an interrupt occurs. The interrupt type of operation results in a highly efficient use of computer time and will permit the simultaneous use of the computer for other tasks such as the modified coresident debugging program used as a housekeeping aid to permit examination and modification of the operating program and the disk system without interference to or from the mass spectrometer system.

The local and remote teleprinter pages provide such services as reading, typing, carriage return-line feed and spacing subroutines, and provide for decoding requests for service made on the two teleprinters.

System Performance. Up to the present time, the system has performed satisfactorily with less than 5% down-time. Most of the down-time was caused by a weak pulse in the skip line causing a disk read error whenever the pulse-height analysis equipment was switched on. Some time was also lost because of the malfunctioning of the high speed reader/punch. Neither of these malfunctions caused any errors in the mass spectrometer system.

Some modifications had to be made in the basic program: adjustment of the number of data points taken to 200/measurement; changing the timing between data points to about 16.7 milliseconds; the number of scans in a set of data; and the settling time after a change in magnet or amplifier setting.

The reliability and stability of the mass spectrometer magnet power supplies and high voltage supplies have been more than adequat. Compensation of magnet hysteresis had to be made by using different settings for the mass-235 peak depending upon whether the magnet current was being increased or decreased.

The reliability of the data produced is illustrated by the five analyses of NBS-900 standard material shown in Table 1. The standard deviation is about 0.02% and the bias in the U-235 value is -0.016%. Manual operation gives limits having the same order of magnitude.

A typical analysis involving the stepping through a preset sequence of peaks and backgrounds, with slight variations for each instrument, selecting the proper amplifier ranges, and calculating the results, takes about 6 to 8 min., essentially the same time as is needed for manual operation. However, the operator now knows immediately if the run is satisfactory and can either repeat the analysis or shut down the instrument. With the elimination of the tedious chart measurements and lengthy manual calculations, sample through-put increases and more time is available for developmental and other studies. Operator acceptance of the system is good.

REFERENCES

1. Nelson, L. C., Jr. and Hemmer, R. J., "A Computer Controlled Isotope Ratio Mass Spectrometer Using Dry Reed Relays," Proceeding, DECUS, Spring, 1969 Symposium, Maynard, Mass., 1969, p. 201.

2. Williamson, F. K., "D-Bug," DECUS Program Library No. 8-105, (September 1967).

TABLE 1

REPRODUCIBILITY FOR FIVE RUNS ON NBS-900 STANDARD

U-234

0.7808 0.7745 0.7763 0.7796 0.7809

* SAMPLE NO	SIZE	MEAN	VARIANCE	STAND. DEV.
1	5	+0.7784199E+00	+0.8225440E-05	+0.2868002E-02

U-236

0.3375 0.3374 0.3359 0.3358 0.3359

* SAMPLE NO	SIZE	MEAN	VARIANCE	STAND. DEV.
2	5	+0.3364999E+00	+0.7450580E-06	+0.8631673E-03

U-238

8.790 8.819 8.809 8.825 8.773

* SAMPLE NO	SIZE	MEAN	VARIANCE	STAND. DEV.
3	5	+0.8803199E+01	+0.4730224E-03	+0.2174907E-01

U-235

C90.00000
90.0919 90.0688 90.0785 90.0600 90.1103

* SAMPLE NO	SIZE	MEAN*	VARIANCE	STAND. DEV.
4	5	+0.9008190E+02	+0.3923997E-03	+0.1980908E-01

* VALUE OF STD./MEAN VALUE = 90.0970/90.0819 = 1.0016

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

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

One of the factors limiting the sample analysis rate of thermal-ionization-source mass spectrometers is the time required to attain a satisfactory vacuum after a sample change. The use of large capacity pumps is the obvious first step in the reduction of pump-down times. Another step would be to reduce the volume which is vented to atmospheric pressure during a sample change. This can be accomplished by valving off as much of the system as possible before venting. The most effective way, however, of reducing sample change time is the use of a vacuum lock. A vacuum lock reduces the volume which must be evacuated to a minimum and allows one to insert a sample into the vacuum system without disturbing the vacuum significantly.

Design

There are numerous types of vacuum locks in use since the design must reflect the needs of a particular system. A lock which has been designed at the New Brunswick Laboratory (NBL) for use on a 12-in. radius multiple-filament-source mass spectrometer is shown in Figure 1.

The vacuum lock consists of a sample insertion bar, which is supported by "O"-rings fitted into the wall of an evacuation cylinder, and a 2-in. gate valve, located between the source housing and the evacuation cylinder, to isolate the source region when a sample is changed.

The sample is mounted on the end of the sample insertion bar (Figure 2). A standard filament holder, which supports the ionizing filament and the filaments on which the sample is evaporated, plugs into a ceramic block attached to the bar with 1-in. long ceramic insulators. Electrical power to the filaments is supplied via extensions of the filament studs which extend from the ceramic block and make contact with receivers mounted on the first source plate when the bar is inserted. Contact is made during the last 1/4-in. travel of the bar. Dowel pins mounted on the first plate fit into holes in the filament holder to assure proper alignment of the filaments. The inside of the source housing with the vacuum lock removed is shown in Figure 3.

The vacuum system of the lock is very simple. It has been found that no differential pumping is required across the "O"-ring located between the pump-out ports so that only one rotary pump is required. A 70-l./min. pump is presently used. Only two valves are required in the pumping system: a rotary pump isolation valve, and an air inlet valve to vent the lock when changing a sample. Both valves are manually operated.

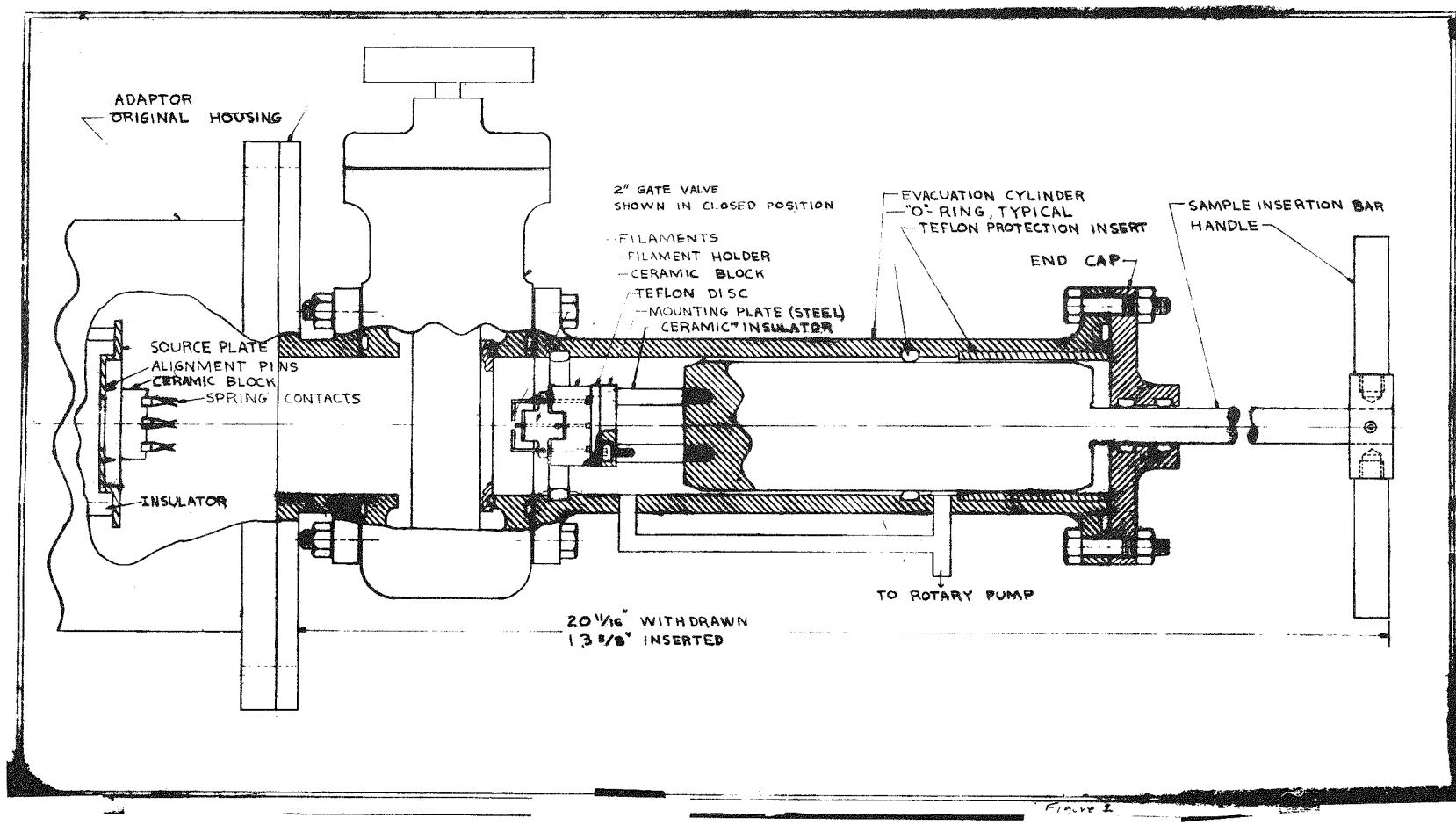

FIGURE 1. VACUUM LOCK

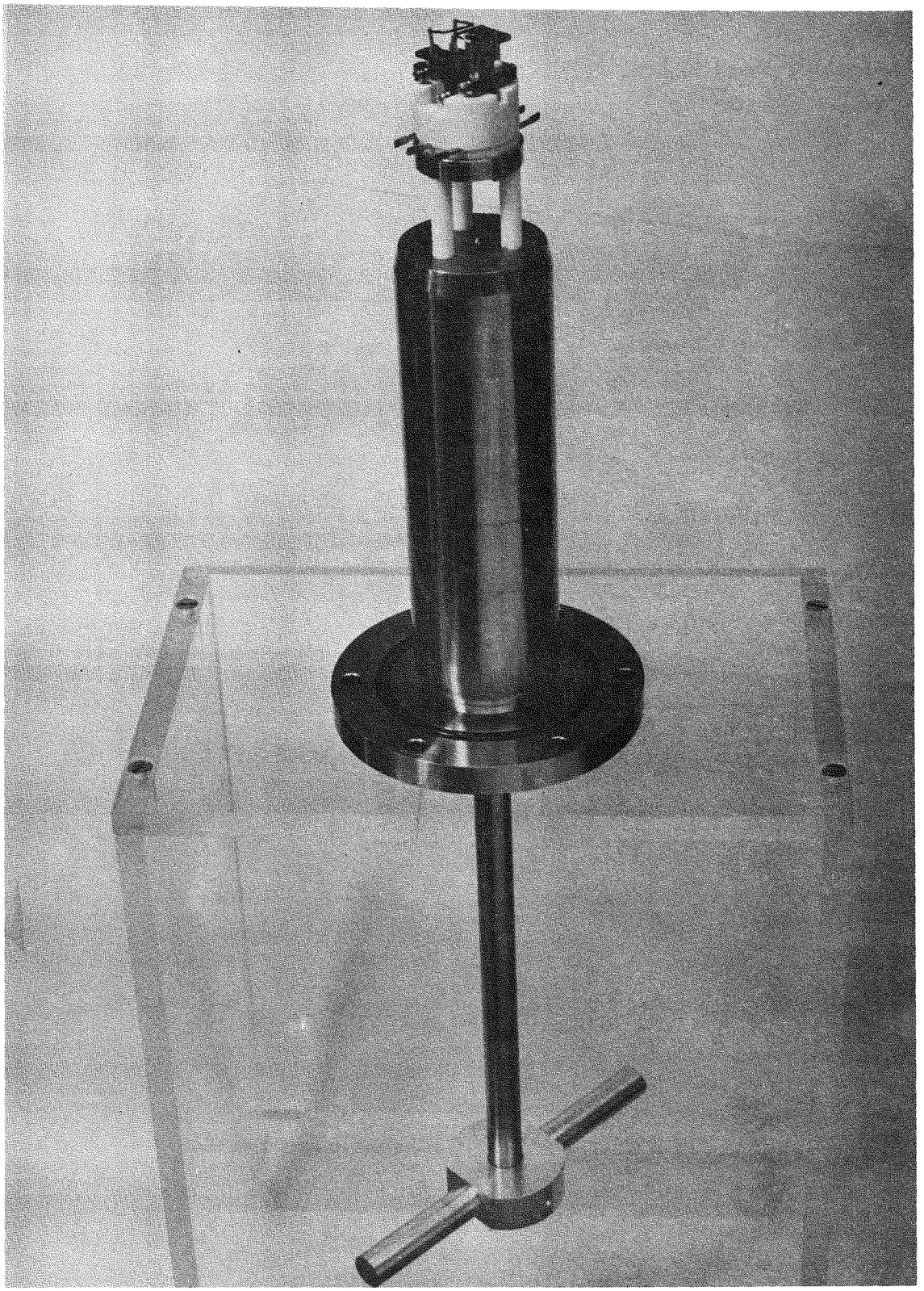

FIGURE 2. THE SAMPLE INSERTION BAR MOUNTED IN A HOLDER DURING A SAMPLE CHANGE

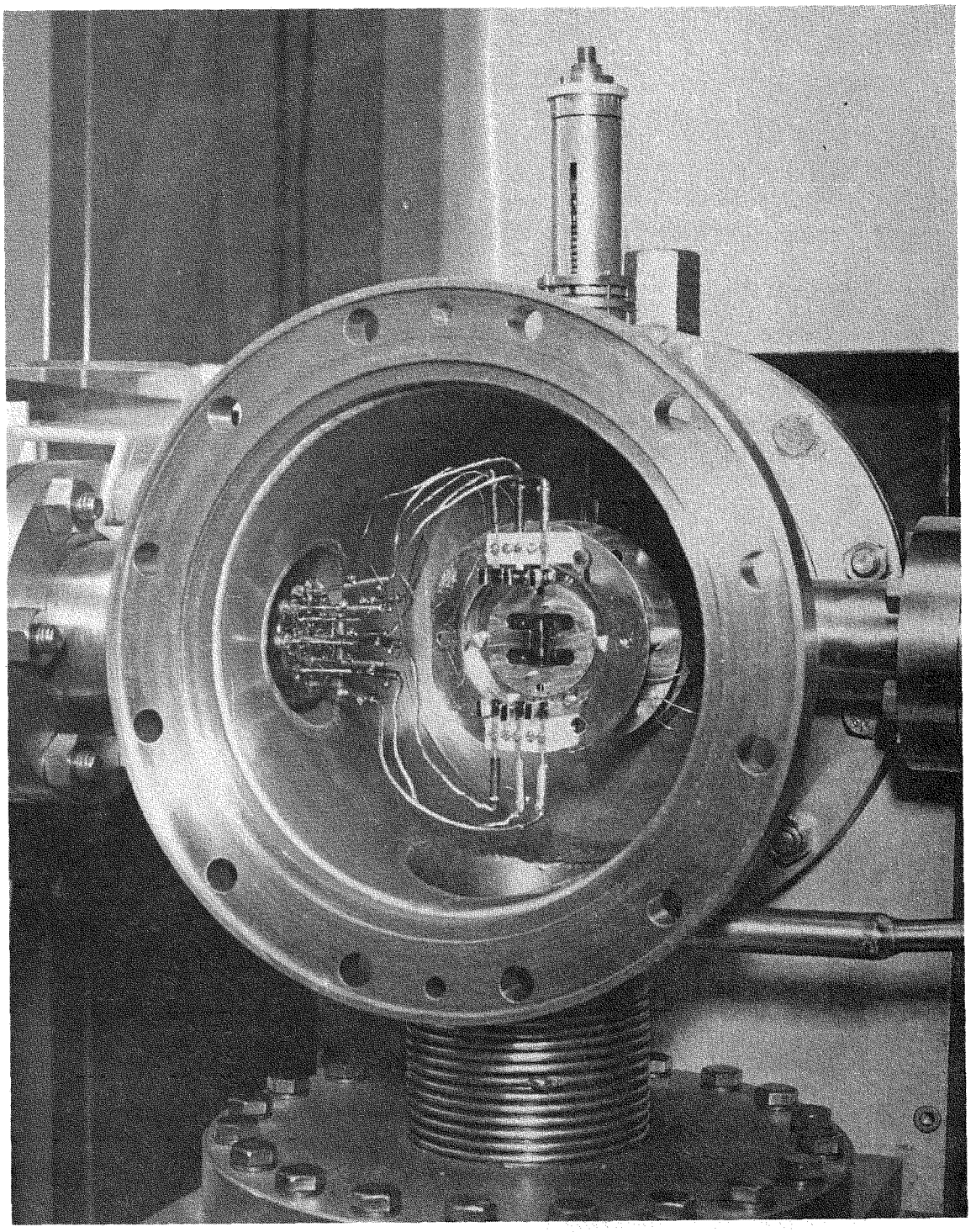

FIGURE 3. THE INSIDE OF THE SOURCE HOUSING WITH THE VACUUM LOCK REMOVED

The vacuum lock was designed to make use of as much existing equipment as possible. The gate valve, for example, was already on hand. The filament holders used with the lock are the same as those used in the three other mass spectrometers in operation at the laboratory. The only modification to the instrument itself was the addition of the contacts to the first source plate to supply power to the filaments.

Operation

The operation of the vacuum lock is described. When it is necessary to insert a new sample, the sample insertion bar is withdrawn until its large diameter section contacts the end cap. The gate valve is closed, the rotary pump isolation valve closed, and the air inlet valve opened. The sample insertion bar and the end cap are withdrawn completely and placed in a holder, as shown in Figure 2. The filament holder is grasped with pliers and removed from the ceramic block. A new filament holder with a fresh sample is plugged into the block. The sample insertion bar is inserted into the evacuation cylinder. One or two bolts can be placed in the end-cap flange or it can be manually held in position while the air inlet valve is closed and the rotary pump isolation valve is opened. After this valve is opened, atmospheric pressure is sufficient to hold the end cap in place. The lock is shown in the pre-pumping stage in Figure 4.

When the pressure in the cylinder reaches 10^{-2} torr (about 3 min.), the gate valve is opened and the bar pushed in. The source region is exposed to the rough vacuum in the cylinder until the bar contacts the "O"-ring nearest the gate valve. This step causes a surge in the source region pressure, but the pressure returns to its normal operating value of 10^{-6} torr in a few seconds.

The bar is pushed in as far as possible. The bar stops when the filament holder contacts the source plate. The lock is shown in this position in Figure 5. Voltage may now be applied to the filaments and analysis of the sample begun. The time required, from extraction of the old sample to application of voltage to the filaments of the new sample, is about 5 min.

DISCUSSION

The vacuum lock has been in operation for about 3 months and no major problems have been encountered in its operation. No hydrocarbon background has been observed in the spectrum from the vacuum grease used to lubricate the insertion bar and "O"-rings. Samples analysis times have been reduced by 50%, from 1 hr. to 30 min., by use of the lock. Two additional advantages of the lock are: the accelerating voltage (14 kV) no longer has to be turned off during a sample change, and hence requires no re-stabilization time; the operating pressure of 10^{-6} torr in the source region is lower than that of 2×10^{-6} torr when the vacuum lock is not used.

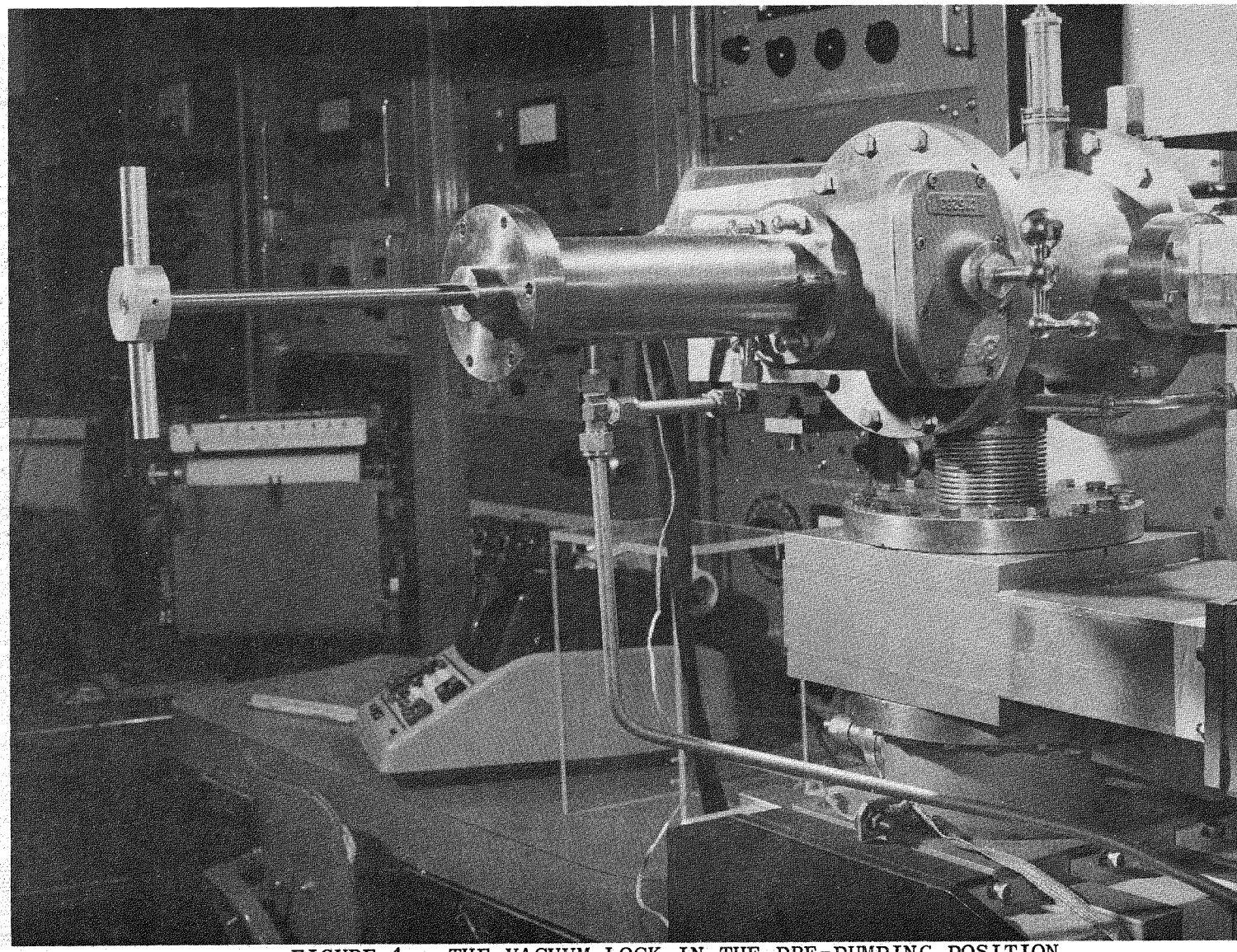

FIGURE 4. THE VACUUM LOCK IN THE PRE-PUMPING POSITION

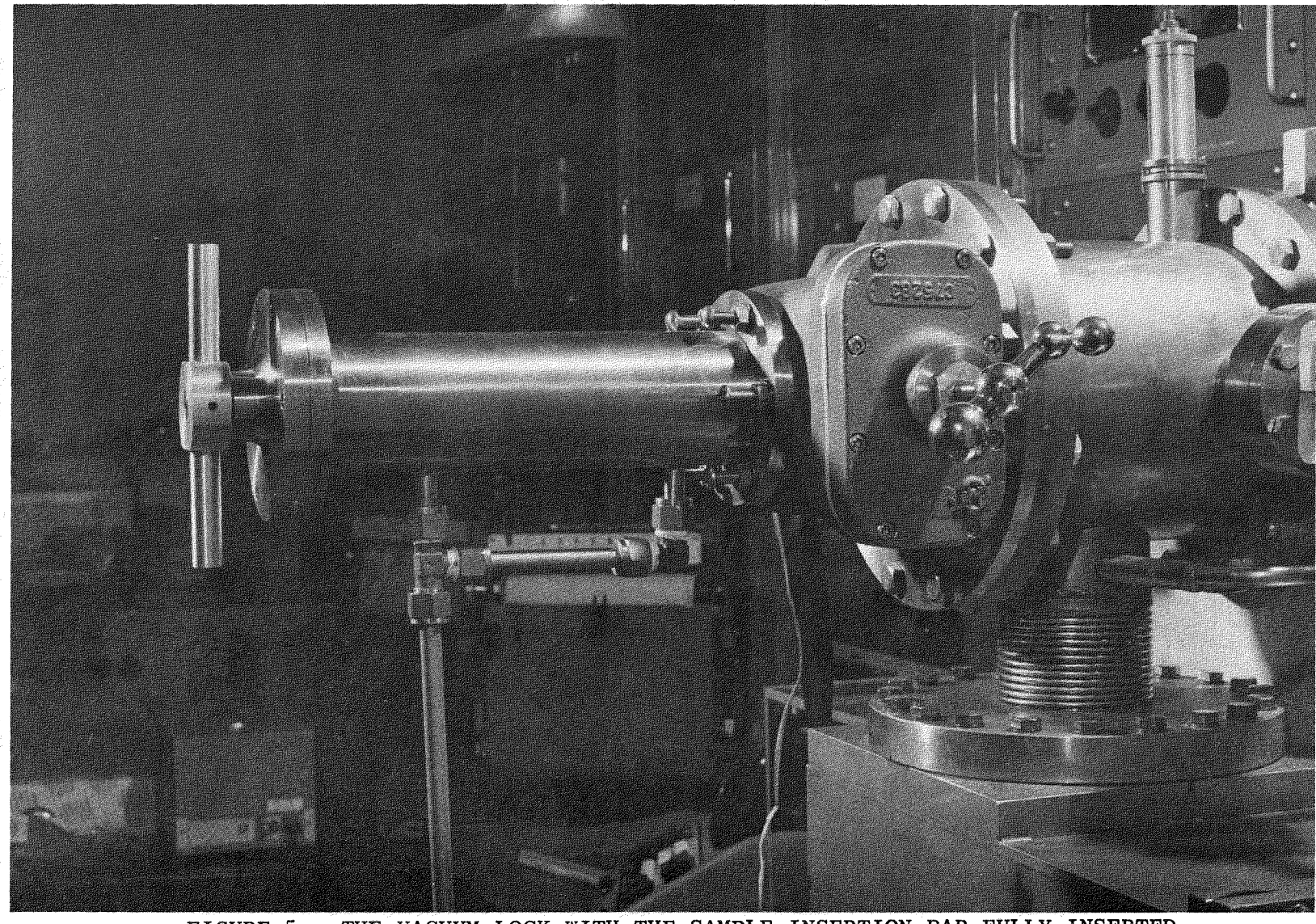

FIGURE 5. THE VACUUM LOCK WITH THE SAMPLE INSERTION BAR FULLY INSERTED

SOLID-STATE VERSIONS OF THE OAK RIDGE NATIONAL LABORATORY (ORNL) MODELS Q-2564 AND Q-2005 CONTROLLED-POTENTIAL COULOMETERS

Ralph Hemmer

The ORNL controlled-potential coulometers models Q-2564 and Q-2005 are vacuum-tube instruments. Two solid state versions of the model Q-2564 and one of the model Q-2005 have been constructed at the New Brunswick Laboratory (NBL) and have been in operation for about three years. In this report, the modifications of the original instruments and the performance of the NBL versions are summarized.

EXPERIMENTAL

In the three instruments constructed at NBL, the original Philbrick USA-3-M3 amplifier is replaced with either a Philbrick SP-656-M or P65A operational amplifier. A Philbrick P66A booster follower is used with either amplifier. The original Philbrick R-100B power supply is replaced with a Philbrick PR-300-C unit to provide the necessary supply voltages. The variable positive or negative 3-volt zener regulated controlled-potential supply and the power supply for the automatic cut-off circuitry are left unchanged. The Meter Range Switch circuitry is modified to include a higher current range as well as a logarithmic position.

A block diagram of one of the modified Q-2564 instruments, designated as Q-2564-1S, is shown in Figure 1. Here, the original Philbrick USA-3-M3 amplifier is replaced directly with a Philbrick SP-656-M operational amplifier. In using this amplifier the current output of the electrolysis cell is increased from 8 to 20 ma. Since the output voltage limit is now 10 volts compared to the 100 volts of the original USA-3-M3, the resistor values for the Microequivalent Range Switch are reduced by a factor of 10.

Figure 2 shows the model Q-2564-2S and indicates how a Philbrick P-66A current booster is added to the current and control amplifiers to obtain a further increase in current capability. The control amplifier is a P-65A differential operational amplifier which compares favorably to the SP-656-M for this function.

A block diagram of the modified model Q-2005 is shown in Figure 3. A high-precision 100-ohm resistor is placed between the reference and controlled electrode for calibration, eliminating the need for an external battery circuit.

When the P-66A current booster was initially added to raise the current capability from 20 to 100 ma. it was found that both the SP-656-M and P-65A amplifiers reach their maximum output voltage of 10 volts at 60 ma. By reducing the voltage gain of the circuit, an output of 100 ma. is available. To protect the circuits

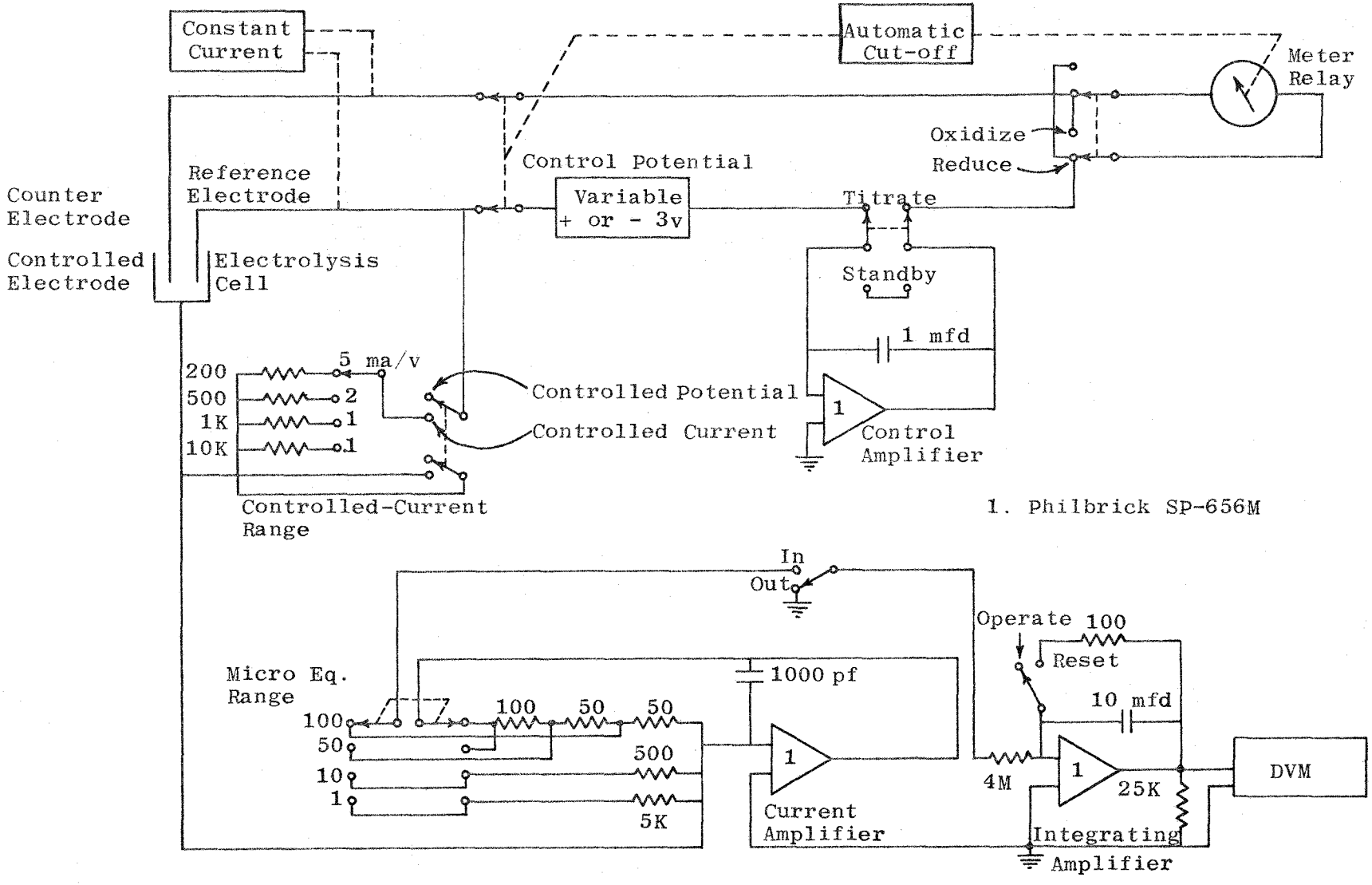

FIGURE 1. SOLID STATE Q-2564-1S

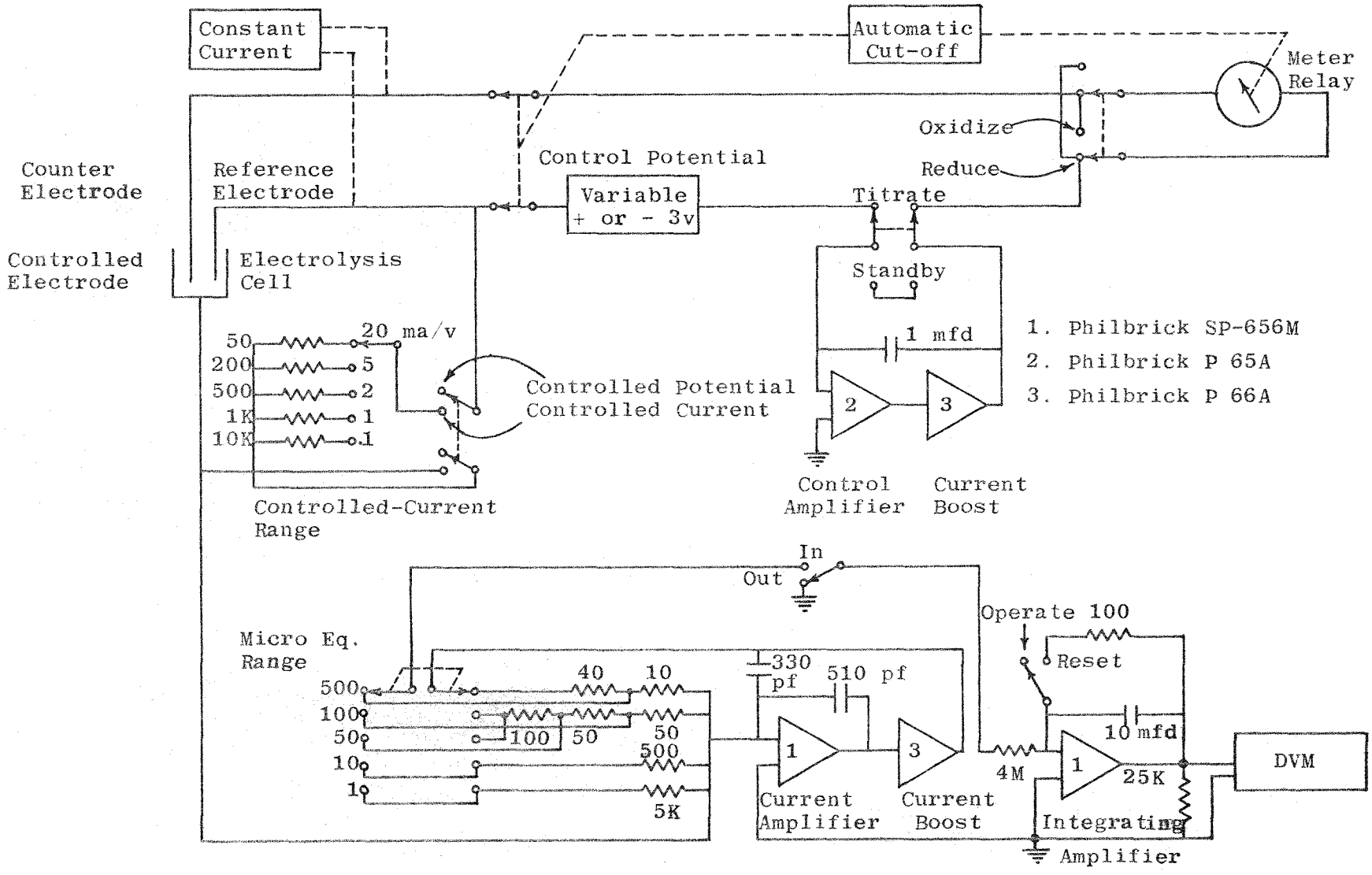

FIGURE 2. SOLID STATE Q-2564-2S

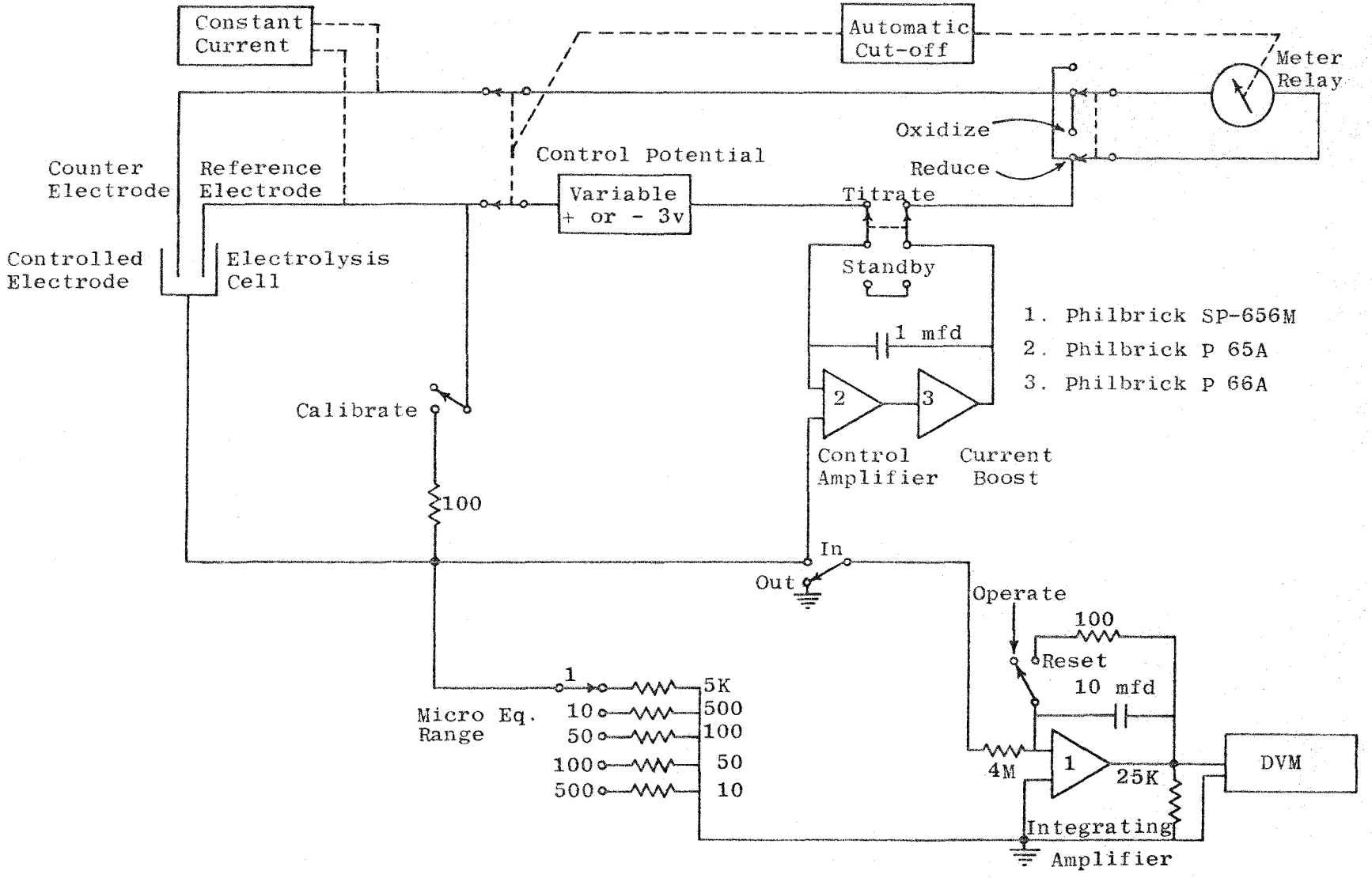

FIGURE 3. SOLID STATE Q-2005

from overload, an overload circuit sensitive to a positive or negative 10 volts is placed across the output of each amplifier. A front panel light is used with each overload circuit.

The readout device for each of the three instruments is a Non-Linear Systems Model X-1 digital voltmeter. With a readout of 10.0000 volts and an input impedance of 10^{10} ohms, accurate voltage readings in the coulometer can be read without loading the circuits. A front panel switch permits the integrator output, the current amplifier output, the voltage across the controlled-current range resistors, the potential between the controlled and reference electrodes, and the control potential to be read.

As can be seen on the block diagrams, the instruments can be used in the constant-current mode. The calibrate switch on the modified model Q-2005 acts in the same manner as the Controlled-Current Range Switch on the modified Q-2564 models. Any desired range can be obtained by adding more resistors. By shorting the counter and reference electrodes, the instruments can be calibrated at any current level.

RESULTS AND CONCLUSION

In three years of operation the only electronic failures have been the SP-656-M amplifiers which use a mechanical chopper that needs replacing generally after two years of continuous operation. This failure rate represents an improved reliability over that shown by the vacuum-tube Model Q-2005.

These solid-state instruments show, in addition to the advantages of smaller size, less power consumption, less heat evolution, and low long-term drift of the current and integrating amplifiers. Short-term drift of the control amplifiers and the control potential is less than 0.1 mv./day.

Because of the slight corrosive atmosphere in the laboratories housing the instruments, the silver contacts of the open-type wafer switches caused intermittent functioning after a few months of operation. A change to sealed wafer switches has corrected this problem.

Calibration of the instruments can be carried out by connecting the counter and reference electrodes together and placing the instrument in the controlled-current mode. A typical response of all three instruments is illustrated by the performance of the modified model Q-2564, Table 1.

TABLE 1

CALIBRATION OF SOLID STATE INSTRUMENT, MODEL Q-2564-1S

Range, μeq.	Controlled Current Range, ma./volt	Controlled Potential, volts	Time, sec.	Current, ma.	Integrator Output,[a] volts	C.V., %
100	5	1.0000	200	5	1.2592	0.011
50	5	1.0000	200	5	2.5184	0.013
10	1	0.5000	400	0.5	2.5168	0.010
1	1	0.2500	200	0.25	6.2964	0.030

a. average of 5 determinations

The electrical calibration factor in volts/coulomb may be calculated from the data in Table 1 by the expression

$$F = V/IT$$

Where: F = volts/coulomb,

V = the integrator output in volts,

I = the current in amps.,

and T = the time in sec.

The microequivalent ranges are supposed to be exact multiples of each other and a comparison of the data in Table 2 indicates that this is the case.

TABLE 2

CALCULATED VOLTS/COULOMB VALUES - MODEL Q-2564-1S

Range, μeq.	F, volts/coulomb	Comparison of Range x F
100	F_1 = 1.2592	125.92
50	F_2 = 2.5184	125.92
10	F_3 = 12.584	125.84
1	F_4 = 125.93	125.93

Weighted average = 125.90

C.V., % = 0.033

Chemical calibrations of the Q-2564-1S instrument, carried out routinely with standards prepared from National Bureau of Standards plutonium sulfate, NBS 944, and plutonium metal, NBS 949b, typically yield results as follows:

Electrolyte:	1M $HClO_4$ + 0.02M sulfamic acid
Reduction Potential:	+0.56 volts vs. S.C.E.
Oxidation Potential:	+0.88 volts vs. S.C.E.
Cut-Off Current:	30 μa.
No. of Determinations:	7 (4-NBS 944, 3-NBS 949b)
Chemical Calibration:	1.0102 volts/mg., C.V., = 0.051%

When this calibration value is used to analyze a known solution containing about 2 mg. of plutonium, the coefficient of variation of 9 measurements is approximately 0.03% and the relative error is -0.03%.

Table 3 shows a comparison between the coulometric and chemical analysis of four samples of mixed oxide, UO_2-PuO_2.

TABLE 3

COMPARISON OF COULOMETRIC AND CHEMICAL ANALYSES - MODEL Q-2564-1S

Plutonium, mg./g.		Relative
Coulometric	Chemical[a]	Difference, %
2.5312	2.5329	-0.07
2.2882	2.2886	-0.02
2.6126	2.6085	+0.16
2.3069	2.3091	-0.10

a. Jones reductor, dichromate titration with constant-current potentiometric endpoint.

The constant current mode of the instrument was evaluated by titrating standard arsenious oxide with electrogenerated iodine (10 ma.) and biamperometric endpoint detection at two platinum electrodes, Table 4. The final readout is taken from the integrator, precluding the necessity of measuring exactly the current or the timer.

TABLE 4

TITRATION OF ARSENIOUS OXIDE WITH ELECTROGENERATED IODINE

As_2O_3, mg.		
Taken	Found	Error, %
1.9042	1.9043	+ 0.005
1.4647	1.4638	- 0.06
1.2575	1.2587	+ 0.10
1.0579	1.0577	- 0.02
1.2181	1.2174	- 0.06
1.2245	1.2250	+ 0.04

Digital panel meters are presently available which read to 4.0000 volts. These meters are reasonable replacements for the digital voltmeters at a reduction of cost and space. The production of Philbrick SP-656M amplifiers have been discontinued. They will be replaced by newer units that use a solid-state chopper instead of the mechanical type. This improvement should further materially decrease the currently very low down-time of the instruments.

ACKNOWLEDGMENT

Dr. K. Lewis of the NBL Analytical Development Section supplied the evaluation data used in this report.

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