01-173

UCRL-52060

**STUDIES OF FACTORS AFFECTING URANIUM
DETERMINATIONS BY AUTOMATED COULOMETRIC
TITRATION (NEW BRUNSWICK LABORATORY/
DAVIES-GRAY METHOD)**

J. E. Harrar and W. G. Boyle

April 26, 1976

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

**LAWRENCE
LIVERMORE
LABORATORY**
University of California/Livermore

MASTER

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$; Microfiche \$2.25

<u>Page Range</u>	<u>Domestic Price</u>	<u>Page Range</u>	<u>Domestic Price</u>
001-025	\$ 3.50	326-350	10.00
026-050	4.00	351-375	10.50
051-075	4.50	376-400	10.75
076-100	5.00	401-425	11.00
101-125	5.25	426-450	11.75
126-150	5.50	451-475	12.00
151-175	6.00	476-500	12.50
176-200	7.50	501-525	12.75
201-225	7.75	526-550	13.00
226-250	8.00	551-575	13.50
251-275	9.00	576-600	13.75
276-300	9.25	601-up	*
301-325	9.75		

*Add \$2.50 for each additional 100 page increment from 601 to 1,000 pages:
add \$4.50 for each additional 100 page increment over 1,000 pages.

LAWRENCE LIVERMORE LABORATORY

University of California Livermore, California 94550

UCRL-52060

**STUDIES OF FACTORS AFFECTING URANIUM
DETERMINATIONS BY AUTOMATED COULOMETRIC
TITRATION (NEW BRUNSWICK LABORATORY/
DAVIES-GRAY METHOD)**

J. E. Harrar and W. G. Boyle

MS. date: April 26, 1976

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees nor any of their contractors, subcontractors, or their employees make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

Contents

Abstract	1
Introduction	1
Study No. 1: Detecting Vanadium(V) in Vanadyl Sulfate Diluent	3
Study No. 2: Loss of Uranium(IV) After Dilution	5
Study No. 3: Comparison of Experimental with Theoretical Titration Curves; Determination of End-Point Error	5
Study No. 4: Current-Potential Characteristics of Generator Electrode; Titration/Current Efficiency	11
Study No. 5: Effect of Phosphoric Acid Impurities on Operating Potential of Generator Electrode	13
Study No. 6: Reproducibility of Reagent Solution Delivery	16
References	20
Appendix: Procedure for Testing VO_2SO_4 Solution for Vanadium(V) by Controlled-Potential Coulometry	22

STUDIES OF FACTORS AFFECTING URANIUM DETERMINATIONS BY AUTOMATED COULOMETRIC TITRATION (NEW BRUNSWICK LABORATORY/DAVIES-GRAY METHOD)

Abstract

Our work is part of a project to develop a computer-automated system based on the New Brunswick Laboratory/Davies-Gray method for coulometric titration. For this particular set of studies, we intended to define the method's errors to ascertain its absolute accuracy.

We developed an analytical technique to examine vanadyl sulfate diluent for vanadium(V). None could be found in any of the lots tested. Certain lots of reagent-grade phosphoric acid contained an unidentified impurity that caused high generator-electrode potentials and a positive error. We measured the current-potential characteristics of the generator electrode. The data

indicated that a significant fraction of uranium(IV) was oxidized directly during the early stages of titration. Using equations theoretically applicable to such a titration, we found a negligible difference between the inflection point of the titration curve and the equivalence point in the titration. However, the actual experimental curves did not agree with the theoretical curves early in the titration.

Measurements of the background current indicated a level equivalent to ~0.2 mg uranium. Our evaluation of the reagent delivery system used in the automated analyzer revealed adequate reproducibility.

Introduction

The Lawrence Livermore Laboratory (ILL) has a project to develop a computer-automated system for the determination of the amount of uranium in solution. This system is based on the coulometric titration method of Goldbeck and Lerner¹⁻⁴ of the New Brunswick Laboratory (NBL).

Basically, this method involves:

- Reduction of uranium(VI) to uranium(IV) by reaction with iron(II) in strong phosphoric acid (H_3PO_4).
- Oxidation of excess iron(II) by reaction with nitric acid

(HNO₃) catalyzed by molybdenum(VI).

- Titration of uranium(IV) with vanadium(V), which is electrogenerated at controlled current.

The coulometric procedure is an extension of the volumetric method developed by Davies and Gray⁵ and refined by Eberle, et al.⁶ at NBL.

We have developed the equipment and instrumentation⁷ for automatically determining uranium. Our system can perform sample changing, pretitration reagent addition, titration, titration-curve data logging, end-point calculation, result readout, and posttitration solution disposal.

A method to determine uranium would be most useful if it involves no systematic error (bias). If the coulometric titration could be placed on an absolute basis, calculations of uranium quantities could be based solely on the electrical calibrations of the instrumentation. This would reduce the systematic error. Apart from the possibility of compensating errors, a bias-free determination would require:

- Accurate chemical preparation of uranium for titration.
- Negligible loss of uranium(IV) before completion of titration.
- Chemical and electrochemical

equilibrium in the titration mixture when titration is completed (or end point reached).

- No intrinsic difference between the assumed end point and the true equivalence point.
- One-hundred percent current or titration⁸ efficiency in the controlled-current electrolysis.
- Negligible errors in control of the current.
- Negligible timing errors.

Our main goal was to define the errors in the automated coulometric titration method to ascertain its absolute accuracy. To this end, six ministudies were conducted to examine (in more detail than before) some of the factors affecting the method's accuracy. We also examined several characteristics of the automated system as they relate to the coulometric titration.

The very high accuracy and precision of the volumetric procedure, as carried out with potassium dichromate (K₂Cr₂O₇) titrant,^{5,9} provide ample evidence that reduction of uranium(VI) to uranium(IV) is complete. These studies also showed that the iron and nitric acid-molybdenum(VI) reagents cause no errors.

Study No. 1: Detecting Vanadium(V) in Vanadyl Sulfate Diluent

In the volumetric procedure, vanadyl ion [vanadium(IV)] is added to the uranium(IV) solution to accelerate the attainment of equilibrium in the titration.⁶ This is also the precursor species from which the vanadate ion [vanadium(V)] is electrogenerated in the coulometric procedure. Since vanadium(V) reacts directly with uranium(IV), its presence in the vanadyl sulfate (VOSO_4) diluent added to the solution before titration would create a negative bias in the uranium determination. The $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ salt used to prepare the diluent may contain vanadium(V). Also, vanadium(V) may arise from air oxidation of the vanadyl ion (VO^{2+}) in the diluent. Eberle and Lerner¹⁰ previously investigated the latter effect.

To test for the presence of vanadium(V) in VOSO_4 , we developed a controlled-potential coulometric (CPC) procedure that involves the reduction of vanadium(V) to vanadium(IV) in 1.5 M H_3PO_4 . The appendix details this procedure, which is based on a previously published method¹¹ that uses a platinum-working-electrode cell. Since each determination has a sensitivity of ~ 0.03 mg vanadium(V) and ~ 375 mg vanadium(IV) is tested, the procedure can

detect a level of $\sim 0.01\%$ vanadium(V). In the controlled-current coulometric method for uranium, in which 160 ml of a 0.025 M VOSO_4 solution is added, the sensitivity of the CPC procedure is equivalent to ~ 0.04 mg uranium. Thus, a bias from this source should be detectable at this level.

We used the CPC procedure to test seven different lots of Fisher Scientific Company catalog number V-8 $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ of various ages (704634, 710500, 722508, 730999, 732426, 736791, and 790998) and one seven-year-old sample of Research Organic-Inorganic Chemicals catalog number VI7 $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$.^{*} We found no evidence of vanadium(V) in any of the material. There are strong oxidants other than vanadium(V) that could cause a bias in the uranium method, but most of these would also be detected in the CPC test.

Eberle and Lerner¹⁰ found that vanadyl solutions aged in air caused a negative bias when used in the uranium determination. They found

^{*}Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

spectrophotometric evidence of vanadium(V) in these solutions within a few hours of preparation. On the same basis as our test, they found a level of 0.25 mg uranium equivalent in the freshly prepared solution.

The appearance of vanadium(V) in solution is presumably due to one or both of the reactions

depending on the extent to which oxygen is reduced. It can be postulated that, in either case, the addition of acid to the diluent containing VO^{2+} should aid in stabilizing the VO^{2+} against air oxidation. In the original volumetric method⁶ and in the tests on the diluent conducted by Eberle and Lerner,¹⁰ there was no acid in the diluent. However, in the Fisher Titralyzer adaptation of the volumetric method,⁶ and in the original coulometric method,¹ the diluent was made 1 M in sulfuric acid (H_2SO_4). In a later adaptation of the coulometric method for automatic operation,² the diluent was 0.18 M H_2SO_4 .

To test the stability of the diluent as a function of acid concentration, we prepared three solutions of 0.025 M VOSO_4 , placed them in 250-ml open beakers, and allowed them to stand at 20 to 26°C for three months. During this time, evaporative losses were replaced by water. At the end of this time, the vanadium(V) in the solution was determined by the CPC procedure.

Table 1 shows the results.

Table 1. Quantity of vanadium(V) in diluent after standing in air for 3 mo. Lot number 730999 $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$.

Acid concentration (M)	Vanadium(V) found (mg U equivalent/160 ml diluent)
0	4.4
0.18	0.51
1.0	0.44

The data clearly show that acid decreases the rate of oxidation of the vanadium(IV). As a parallel experiment, we also studied the quantity of vanadium(V) appearing in the diluent used in the LLL computer-automated titration system. After two months use, during which time the 0.18 M H_2SO_4 diluent was intermittently under 83 kPa (12 psi) pressure

of air, the mg uranium equivalent/
160 ml was 0.60 mg.

As a result of these experiments, for the LLL titration system we decided to make the concentration of H_2SO_4 in the diluent 0.30 M and pressurize the reagent containers with nitrogen or other inert gas rather than air. Nevertheless, it

should still be possible to use air without error, if the diluent is consumed and replaced at frequent intervals. It also appears feasible to increase the concentration of vanadium(IV) in the diluent. A benefit of this would be a decrease in the generator-electrode potential required to maintain a given level of constant current.

Study No. 2: Loss of Uranium(IV) After Dilution

Loss of uranium(IV) after the dilution step, due to oxidation by HNO_3 , places an upper limit on the allowable titration time. An adequate discussion of this effect appears in two NBL publications.^{1,6} Another possible source of uranium(IV) loss, diffusion of the species into and through the counter-electrode separator

material, has not been investigated but is believed to be of minor importance. The solution contacts the separator only during the titration step, which never exceeds the allowable maximum time of ~8 min. Determinations using both a Nafion ion-exchange membrane tube¹² and a porous Vycor tube revealed no difference in recovery.

Study No. 3: Comparison of Experimental with Theoretical Titration Curves; Determination of End-Point Error

Previous applications of the determination of uranium by the Davies-Gray method and its extensions,^{1-4,6} where potentiometric end-point detection was used, have been based on the end point as the point of maximum slope ("inflection point") of the titration curve. Apart from the question of whether or not the inflection point is accurately

detected, we would like to know whether or not it actually coincides with the true equivalence point in theory for redox reactions of this type. Such intrinsic errors, albeit small, exist^{13,14} for many such reactions. Knowledge of the theoretical titration curve for our particular case (uranium/vanadium reaction) is needed to further establish that the

coulometric titration can be placed on an absolute basis. One does not need this information for procedures in which the titrant is not a primary standard.

Table 2 shows the approximate composition of the titration medium, assuming the compositions of the reagents given and a "pure" uranium sample. For the species involved in

Table 2. Composition of reagents and final titration solution.

Component	Composition	Volume (cm ³)
Sample	0-18 <u>M</u> H ₂ SO ₄ , 10-200 mg U	15
Reagent 1	1.5 <u>M</u> sulfamic acid	5
Reagent 2	13.3 <u>M</u> H ₃ PO ₄ , 0.11 <u>M</u> Fe(II), 0.001% Cr	45
Reagent 3	8.0 <u>M</u> HNO ₃ , 0.15 <u>M</u> sulfamic acid, 0.4% ammonium molybdate	10
Diluent	0.3 <u>M</u> H ₂ SO ₄ , 0.025 <u>M</u> VOSO ₄	160
		235
Titration solution	2.5 <u>M</u> H ₃ PO ₄	
	0.34 <u>M</u> HNO ₃	
	0.2-1.1 <u>M</u> H ₂ SO ₄	
	0.04 <u>M</u> sulfamic acid	
	0.02 <u>M</u> Fe(III)	
	0.017 <u>M</u> V(IV)	
	0.2-4.3 <u>mM</u> U	
	small amts of Mo, Cr	

this titration, H_3PO_4 primarily determines the formal potentials and equilibria in the reaction system. The overall reaction in the titration is

For the vanadium half-reaction, interpolating the data of Astakhina and Gurevich¹⁵ for H_3PO_4 gives a value of $E^{\circ'} = +0.98$ V vs SHE for 2.5 M H_3PO_4 , where $E^{\circ'}$ is the formal potential. Similarly, Marcus' data¹⁶ yields a value of $E^{\circ'} = +0.52$ V vs SHE for the UO_2^{2+}/VO^{2+} couple in 2.5 M H_3PO_4 .

To determine whether the true equivalence point of the titration coincides with the inflection point of the titration curve, one must construct a theoretical curve of the fraction or percentage of substance titrated vs the solution redox potential (which, experimentally, is measured with the indicator electrode). Goldman derived an equation (Eq. 53 in Ref. 17) appropriate for this purpose:

$$f = \frac{1 + k \cdot \exp(n_1 \psi)}{1 + k \cdot \exp(-n_2 \psi)} + \alpha_R (n_1/n_2) k \cdot \exp(n_1 \psi), \quad (4)$$

which applies to the following theoretical reaction:

In this reaction, the subscripts 1 and 2 refer to the half-reactions of the titrant (vanadium) and the substance titrated (uranium), respectively; Ox is the oxidized form and Red the reduced form of the species in the reaction. Thus $n_2 = 2$ and $n_1 = 1$.

The other symbols in Eq. (4) have the following meanings and values:

$$f = \text{fraction of substance titrated} \\ = 1 \text{ at the true equivalence point}, \quad (6)$$

$$k = \exp \left[- \frac{n_1 n_2}{n_1 + n_2} \cdot \frac{F}{RT} \Delta E^{\circ'} \right], \quad (7)$$

$$\frac{F}{RT} \text{ (from Nernst Eq.)} = 38.923 \text{ at } 25^\circ\text{C}, \quad (8)$$

$$\Delta E^{\circ'} = E_1^{\circ'} - E_2^{\circ'} = +0.98 - (+0.52) \\ = +0.46 \text{ V vs SHE}, \quad (9)$$

$$\psi = \frac{F}{RT} (E - E^*), \quad (10)$$

$$E = \text{solution redox potential}, \quad (11)$$

$$E^* = \frac{n_1 E_1^{\circ'} + n_2 E_2^{\circ'}}{n_1 + n_2} \\ = \frac{1(+0.98) + 2(0.52)}{1 + 2} \\ = +0.67 \text{ V vs SHE} \\ \approx \text{value of } E \text{ at the equivalence point}, \quad (12)$$

$$\alpha_R^\circ = \frac{C_{\text{Red}_1}^\circ}{C_2^\circ}, \quad (13)$$

$$\begin{aligned} C_{\text{Red}_1}^\circ &= \text{initial concentration of reduced form of titrant (VO}^{2+}\text{)} \\ &= 4 \text{ mM/235 cm}^3, \end{aligned} \quad (14)$$

$$\begin{aligned} C_2^\circ &= \text{initial concentration of substance titrated (VO}^{2+}\text{)} \\ &= 0.05\text{--}1.0 \text{ mM/235 cm}^3 \\ &\quad (10\text{--}200 \text{ mg U per sample}). \end{aligned} \quad (15)$$

The above equations are not exact for the vanadium/uranium reaction because, as shown in Eq. (3), hydrogen ions participate in the reaction. Some indication of the effect of H^+ can be obtained by calculating E^* for the complete reaction. The formula is¹⁸

$$\begin{aligned} E^* &= \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_1 + n_2} \\ &+ \frac{x}{n_1 + n_2} \cdot \frac{RT}{F} \log[H^+], \end{aligned} \quad (16)$$

where x is the number of hydrogen ions in the written reaction and $[H^+]$ is the concentration or activity of H^+ . In the titration solution, the total concentration of H^+ is $\sim 8 \text{ M}$. Substituting this into Eq. (16) yields

$$E^* = +0.67 + 0.03 = 0.70 \text{ V vs SHE.} \quad (17)$$

Thus, we see that the concentration of H^+ has a relatively small effect on the theoretical value of the potential at the equivalence point.

This value can be compared with those obtained experimentally:

This work⁷: $+0.78 \pm 0.01 \text{ V vs SHE}$
Goldbeck and Lerner¹: $+0.81 \text{ V}$
Hedrick¹⁹ (volumetric titration):
 $+0.83 \text{ V}$

Even for a reaction that conforms strictly to Eq. (4) and does not involve H^+ ions, the potential (E^*) calculated from Eq. (12) does not coincide exactly with the true equivalence point. This is pointed out by Goldman¹⁷ and is due to the distortion of the curve caused by the presence of, in this case, the precursor vanadium(IV). The effect is small, however. Goldman's equation

$$f(\text{at } \psi=0) = 1 + \alpha_R^\circ (n_1/n_2)k, \quad (18)$$

for the worst case (smallest amount of uranium, $\sim 10 \text{ mg}$) shows that $E = E^*$ at $f = 1.00026$, or slightly beyond the equivalence point. Another possible perturbation on the above equations (volume changes during titration) is not of concern because of the stoichiometry¹⁷ and because this is a coulometric titration without volume changes.

To determine the location of the inflection point of the titration

curve with respect to the equivalence point in the titration, a program was written for a PDP-8/e minicomputer in double-precision FOCAL to evaluate Eq. (4). For a given set of parameters, we incremented E in 1-mV steps and calculated f for each E value through the range of interest. We also calculated the numerical first derivative ($\Delta E/\Delta f$, using the E vs f values) to find the inflection point of the E vs f curve. Table 3 summarizes the results of these calculations. Figure 1 shows a plot of a theoretical E vs f curve.

The data show clearly that, even at the smallest quantity of uranium titrated, the error incurred in assuming the inflection point to be the equivalence point was less than 0.0001 or 0.01%. We also observed experimentally a trend in E at the inflection point (note that

Fig. 1. Theoretical curve for titration of 100 mg uranium(IV) with electrogenerated vanadium(V) at 25°C. $\alpha_R = 8$, $F/RT = 1/0.025692$.

$E^* = 670$ mV) toward more positive values as the sample size increased. However, here again the effect was not very significant. If, with a constant-potential end-point-detection technique, one used an end-point value of 673 mV (suitable for 200 mg uranium) in the titration

Table 3. Fraction of uranium(IV) titrated and solution-redox potential at inflection point of E vs f titration curve.

U titrated (mg)	Inflection point (max $\Delta E/\Delta f$)	
	f	E (mV vs SHE)
200	1.000017	673
100	1.000024	669
10	1.000099	651

of 10 mg uranium, the error would be only +0.02%.

Figures 2 and 3 show two experimental curves obtained for the titration of 124 and 12.4 mg of uranium. We obtained these curves with an incremental plotter interfaced to the system computer.

Fig. 2. Experimental curve for titration of 124 mg uranium(IV). Titration currents: 300 and 30 mA.

Fig. 3. Experimental curve for titration of 12.4 mg uranium(IV). Titration currents: 100 and 10 mA.

The major difference between these experimental curves and the theoretical curve of Fig. 1 is that, in these and all actual titrations at all levels of uranium, there is a gradual change of potential toward more negative values throughout the first half of the titration. The cause of this is not known; however, we believe it is due to a slow equilibration of the indicator electrode with the new solution, after exposure to the more oxidizing potential at the end of the previous titration. After the gold or platinum indicator electrode has soaked in aerated water, the first run of the day also exhibits this behavior.

The nontheoretical shape of the titration curve prior to the end-point region is a primary reason why we did not investigate the Gran-plot technique²⁰ for end-point location. Also, the Gran-plot technique is inherently somewhat arbitrary²¹ in how one extrapolates the linear, antilog segments to find the end point. Once a procedure is adopted, standardized chemically, then used with unknown samples, the Gran-plot method is precise and accurate. However, we desired to place the determination on an absolute basis, subject to as few arbitrary parameters as possible, then ascertain

whether or not there is an inherent bias or error in the determination. So, our approach for end-point detection was to process E vs

coulombs data with an algorithm that yielded the inflection point of the curve, then use that to calculate the quantity of uranium in the sample.

Study No. 4: Current-Potential Characteristics of Generator Electrode; Titration/Current Efficiency

Perhaps the most important factor influencing the accuracy of the determination is the "titration efficiency," which measures how closely the quantity of electricity consumed in electrolysis agrees with the quantity of uranium titrated.⁸ Titration efficiency is thus really a measure, on an absolute basis, of titration accuracy. It depends in part on the "current efficiency" of electrolysis, which in the present work is the agreement between the quantity of electricity consumed and the quantity of vanadium(V) generated.

Goldbeck and Lerner¹ measured the current efficiency for the electrogeneration of vanadium and found it to be $99.97 \pm 0.05\%$. To investigate the characteristics of this electrolysis further, we obtained curves of the generator electrode potential as a function of current level, both in the presence and absence of uranium(IV). Figure 4 shows the results. The solution was that resulting from the addition of the pretitration reagents in the usual manner. The instrumentation

stepped the electrolysis current in 2-mA increments from zero at a rate of 2 steps per second and measured and plotted generator-electrode potential after each increment. Because the potential required to sustain a given current level is lower in the presence of uranium, especially at levels <100 mA, the data clearly show that uranium, as well as vanadium, was oxidized directly at the electrode. Thus the current efficiency for vanadium(V) generation

Fig. 4. Electrogeneration of vanadium(V) from vanadium(IV) in presence and absence of uranium(IV).

is considerably lower than 100% in the presence of uranium, while the titration efficiency is close to 100%.

The direct oxidation of uranium(IV) beneficially keeps the generator-electrode potential lower -- and away from the higher anodic background-current region. However, uranium(IV) contributes less and less to the current as the titration consumes it. Thus, at constant current (e.g., 100 mA), the generator-electrode potential slowly becomes more positive as titration proceeds. (As discussed below, some of this increase is due to the accumulation of an electrolyte impurity on the electrode.).

An indirect, approximate measure of both current efficiency and titration efficiency is the level of background current at the

generator electrode in the potential region where it operates during titration. To the extent that the currents of the primary reactions [uranium(IV) or vanadium(IV) oxidations] and the background current are additive, the latter indicates lowered titration efficiency and a positive error in the determination. Thus, we made measurements of this current under controlled-potential conditions. Table 4 gives these results.

We obtained the Table 4 measurements by connecting controlled-potential coulometric instrumentation²² to the reference, counter, and generator (acting here as the working) electrodes of the titration cell. We set the control potential to the values shown, then carried out

Table 4. Background current and accumulated charge measured under controlled-potential electrolysis conditions.

Potential (V vs $\text{Hg}-\text{Hg}_2\text{SO}_4$)	Current (μA)					Charge (mg uranium equivalent)				
	1 min	2 min	4 min	6 min	8 min	1 min	2 min	4 min	6 min	8 min
+0.20	0									
+0.30	10									
+0.40	25									
+0.50	70	45	32	25	20	0.018	0.023	0.028	0.032	0.036
+0.60	120	110	75	65	55	0.028	0.036	0.050	0.061	0.069
+0.70	450	400	275	220	200	0.075	0.11	0.16	0.20	0.23
+0.80	1800	1500	1200	1000	850	0.22	0.33	0.54	0.69	0.83

electrolysis on the solution resulting from the pretitration reagent addition (except that water was substituted for the diluent). Thus, neither vanadium nor uranium was present. The resulting current was due to electrode surface reactions; impurities in Reagents 1, 2, and 3; and water oxidation. We measured both the electrolysis-current level and accumulated charge (in units of mg of uranium) at the time intervals indicated in Table 4.

The following exemplifies the use of such data. The titration, as normally initiated at 300 mA, requires a generator electrode potential between

+0.65 and +0.75 V vs $\text{Hg-Hg}_2\text{SO}_4$. As discussed in the next section, this potential does not remain constant throughout the titration, rising some 50 to 100 mV as titration proceeds. However, if the potential were to remain constant at, say, +0.70 V, it can be seen from Table 2 that a 6-min electrolysis would entail the accumulation of 0.20 mg-U-equivalent of background charge. These data thus provide some indirect evidence that, even if all other sources of error are eliminated, we can still expect a positive error in titration because of the inherent background current in electrolysis.

Study No. 5: Effect of Phosphoric Acid Impurities on Operating Potential of Generator Electrode

The considerable experience of NBL with the volumetric and coulometric titrations has revealed that reagent-grade H_3PO_4 frequently contains oxidizable impurities. Thus, it is now routine to add $\text{K}_2\text{Cr}_2\text{O}_7$ to H_3PO_4 as a pretreatment procedure before mixing the H_3PO_4 with iron(II) solution. The iron(II) then reduces excess chromium(VI) so the mixture presumably contains no further oxidizable impurities.

This procedure is satisfactory for the volumetric ($\text{K}_2\text{Cr}_2\text{O}_7$) titration, but our present experiments

reveal that $\text{K}_2\text{Cr}_2\text{O}_7$ pretreatment lessens, but does not completely eliminate, an interference in the coulometric titration by a constituent of H_3PO_4 . The interfering substance may or may not be electro-oxidized at the generator electrode; it may be merely adsorbed on the electrode. Its presence causes the potential of the generator electrode (vs that of the reference electrode, as normally measured in the titration system) to be more positive than in its absence or in lower concentration. Although direct oxidation of

the impurity is too small to detect, it indirectly can contribute to a positive error in the titration because the more positive generator-electrode potential means a higher background current in electrolysis (see preceding section).

In addition, this interference has a cumulative or "memory effect." The potential that the generator electrode reaches in a series of equal-quantity titrations increases with each successive titration, suggesting that either the primary contaminant or its reaction product is adsorbed. Soaking of the electrode overnight in water partially, but does not completely, restore the "initial" state* of the electrode. The treatment with HCl, adopted as a standard for the titration system, lowers the generator-electrode potential to a baseline value for the first titration.

Table 5 summarizes the results of a series of experiments to test various samples of H_3PO_4 for their effects on the generator-electrode potential. Before each sample of H_3PO_4 was tested, we cleaned the electrode by boiling it in concentrated HCl. The results show considerable differences among

sources and among different lots of the same manufacturer. Although the Apache Chemical material is reported to be reagent-grade and distilled from Vycor, it did not appear to be of any higher purity than ordinary material. The J. T. Baker sample caused the generator-electrode potential to exceed 800 mV. This produced a black deposit on the electrode, reminiscent of the one observed by Goldbeck and Lerner.¹ This deposit, also visible on some of the cell components, was removable by means of hot, concentrated HCl. Because we found it to be finely divided gold, it appears that the very-positive-potential polarization caused by the impurity causes the generator electrode to undergo a process analogous to platinization of a platinum electrode. This treatment should be avoided at all costs. If an H_3PO_4 sample causes the potential to be too high, it should be discarded immediately.

Electrode poisoning effects of the type found here have also been observed in fuel-cell work involving strong H_3PO_4 .²³⁻²⁵ Oxidizable impurities have been found that inhibit H-atom deposition²³ and the oxidation of hydrocarbons.²⁴ Refluxing of the H_3PO_4 with hydrogen peroxide (H_2O_2) was used in one instance to remove the interference.²³

*The state obtained upon boiling the electrode in concentrated hydrochloric acid (HCl).

Table 5. Maximum generator electrode potential during titrations of ~100 mg quantities of uranium, using different sources of H_3PO_4 .

Source	Potentials, in consecutive runs (mV vs $Hg-Hg_2SO_4$)
Mallinkrodt lot ARJ	669, 690, 694
Mallinkrodt lot VMX	751, 799, 815
Mallinkrodt lot AGK (from NBL)	612, 633, 650
Mallinkrodt lot AGK w/o $K_2Cr_2O_7$	677, 688, 692, 694
Apache Chemical "High Purity"	679, 694 (1st series) 693, 701 (2nd series)
Fisher lot 755162	657, 680
J. T. Baker lot 519873	>800 (Black deposit formed on electrode; after ~12 runs stripped w/hot HCl; found 300 μg Au in soln by atomic absorption spectrophotometry)
British Drug House Analar lot 2063690	692, 749 (Material more viscous than U.S. H_3PO_4 ; only 28 ml vs 45 ml delivered in usual time.)

Bravacos et al.,²⁴ by means of standard addition experiments, concluded that the constituents poisoning their electrodes were phosphorous acid (H_3PO_3) and hypophosphorous acid (H_3PO_2), both of which apparently adsorbed on the

electrode and were oxidized in the potential region of the experiments.

We plan to examine samples of the H_3PO_4 described in Table 5 to try to identify the constituent causing the detrimental behavior.

Study No. 6: Reproducibility of Reagent Solution Delivery

No studies have been carried out to determine the allowable variation in volumes of the four pretitration reagents for the exact conditions of this automated titration. However, previous work on the manual method^{6,26} and recent experience indicate that, at least for chemical reasons, close control is not required.

The sulfamic acid solution volume probably can be $5 \pm 1 \text{ cm}^3$, with an excess probably more tolerable than a deficiency. The same is true of the HNO_3 -molybdenum(VI) reagent, where there must be sufficient solution to destroy the excess iron(II) from the preceding reagent. Here, a volume of $10 \pm 2 \text{ cm}^3$ probably is reasonable. In the case of the iron(II)- H_3PO_4 reagent, there must be sufficient iron(II) to effect rapid reduction of the largest possible quantity of uranium, but not so much that a great excess is present. Also, the volume of solution should not vary so much that it

will affect the mixing characteristics of the solution during the reduction step and/or markedly change the total volume of the final titration mixture. This is also true of the vanadium(IV)- H_2SO_4 diluent, where a relatively small percentage change in volume delivered results in a significant variation in cm^3 of volume. In consideration of this effect, the nominal volumes of the iron(II)- H_3PO_4 and the diluent should be, respectively, $45 \pm 3 \text{ cm}^3$ and $160 \pm 5 \text{ cm}^3$.

Factors that influence the volumes of reagent solutions delivered include driving pressure, variation in the level -- or head -- of solution in the reagent containers, temperature, and changes in flow passages due to accumulation of solid material. Valve wear should not be a factor in affecting solution flow rates. When checking flow rates of reagent solutions, we determined the quantities delivered by weighing the solutions.

The data in Table 6 show that the short-term reproducibility of solution delivery at constant pressure* is well within tolerances. The only variation noted here, occasionally, is a hysteresis in the driving-pressure regulator. This causes the volume delivered to drop slightly on successive deliveries, until the regulator finally responds and bleeds in more gas to restore the driving pressure.

*Effective pressure equals driving pressure minus solution level.

Table 7 shows the effects of a variation in both driving pressure and level of solutions in the containers on the volumes of reagents delivered. The driving pressure is typically held within ± 2 kPa (± 0.3 psi). Thus, this is a minor factor in operating system variation. The solution level, on the other hand, is the most significant variable of all in determining volumes of solutions delivered. The 56-cm change in level for these measurements is equivalent to a pressure change of 5.5 kPa (0.8 psi) for pure water. The effect is within tolerance for all reagents

Table 6. Short-term reproducibility of delivery of reagents [82.8 kPa (12.0 psi) driving pressure].

Weights of solution (g)			
Sulfamic acid	Fe(II)-H ₃ PO ₄	HNO ₃ -Mo(VI)	Diluent
6.048	78.4	12.07	161.3
6.068	79.1	12.10	161.1
6.065	79.3	12.12	160.7
6.058	79.5	12.09	
6.058	79.6		
6.050	79.4		
	77.8		
	77.3		
	77.8		
	78.1		
	78.5		

Table 7. Effects of driving pressure and solution level on volumes of reagent delivered during automatic titration.

Driving pressure, kPa (psi)	Volume delivered, cm ³			
	Sulfamic acid	Fe(II)-H ₃ PO ₄	HNO ₃ -Mo(VI)	Diluent
1-dm ³ solution level				
75.9 (11.0)	4.93	44.7	8.93	148.5
82.8 (12.0)	5.29	49.4	9.68	159.5
89.7 (13.0)	5.66	52.5	10.47	167.9
12-13 dm ³ solution level (3/4-full)				
75.9 (11.0)	5.16	50.4	9.85	155.3
82.8 (12.0)	5.46	56.2	10.50	167.4
89.7 (13.0)	5.85	62.3	11.14	176.0

Change in delivery rate as a function of 56-cm change in solution level, %				
	Sulfamic acid	Fe(II)-H ₃ PO ₄	HNO ₃ -Mo(VI)	Diluent
82.8 (12.0)	3.2	13.8	8.5	5.1

except the very dense iron(II)-H₃PO₄ solution. As a result of these measurements, we reduced the container size for this reagent so the actual level change experienced in the prototype system will be one-half that shown in Table 7.

Table 8 lists some data that illustrate the long-term reproduci-

bility of reagent delivery. We made these measurements without readjustment of the pressure regulator or micrometer valves, the system was in continual use, and the solution levels were at various heights. It appears that, with all the factors involved, we achieved adequate reproducibility in the solution delivery.

Table 8. Long-term reproducibility of reagent delivery. [Pressure: 83.5-81.4 kPa (12.1-11.8 psi), temperature: 22-25°C, head variation: ~30 cm]

Date	Flow rate (g/sec)			
	Sulfamic acid	Fe(II)-H ₃ PO ₄	HNO ₃ -Mo(VI)	Diluent
Oct. 14, 1974	1.375	0.583	0.771	3.75
Oct. 25	1.367	0.598	0.777	3.70
Nov. 1	1.353	0.580	0.761	3.66
Nov. 20	1.405	0.611	0.755	3.64
Dec. 17	1.385	0.600	0.745	3.60
Apr. 29, 1975	1.363	0.546	0.726	3.55
Oct. 13	1.389	0.618	0.749	3.73
Feb. 28, 1976	1.426	0.605	0.733	3.80

References

1. C. G. Goldbeck and M. W. Lerner, Anal. Chem. **44**, 594 (1972).
2. C. G. Goldbeck and M. W. Lerner, in Annual Progress Report for the Period July 1971 to June 1972, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-265 (1972), pp. 5-20
3. C. G. Goldbeck, M. W. Lerner, and G. E. Peoples, in Annual Progress Report for the Period July 1972 to June 1973, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-267 (1973), pp. 29-31.
4. C. G. Goldbeck, in Annual Progress Report for the Period July 1973 to June 1974, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-272 (1974), pp. 36-37.
5. W. Davies and W. Gray, Talanta **11**, 1203 (1964).
6. A. R. Eberle, M. W. Lerner, C. G. Goldbeck, and C. J. Rodden, Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials after Ferrous Ion Reduction in Phosphoric Acid, U.S. Atomic Energy Commission, New Brunswick, N.J., Rept. NBL-252 (1970).
7. J. E. Harrar, W. G. Boyle, J. D. Breshears, C. L. Pomernacki, H. R. Brand, A. M. Kray, R. J. Sherry, and J. A. Pastrone, "An Automated Sample Processing and Titration System for the Determination of Uranium in Nuclear Materials," in Proc. Inst. of Nuclear Materials Management Mtg., Seattle, 1976 (Inst. of Nuclear Materials Management, Manhattan, Kansas, 1976).
8. J. J. Lingane, Electroanalytical Chemistry (Interscience, New York, 1958), 2nd Ed., pp. 488-490.
9. A. R. Eberle and M. W. Lerner, in Annual Progress Report for the Period July 1970 to June 1971, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-262 (1971), pp. 5-16.
10. A. R. Eberle and M. W. Lerner, in Annual Progress Report for the Period July 1969 to June 1970, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-258 (1970), pp. 22-25.
11. L. P. Rigdon and J. E. Harrar, Anal. Chem. **41**, 1673 (1969).
12. J. E. Harrar and R. J. Sherry, Anal. Chem. **47**, 601 (1975).
13. J. A. Goldman, J. Electroanal. Chem. **14**, 373 (1967); **18** 41 (1968).
14. J. A. Goldman, J. Electroanal. Chem. **18**, 41 (1968).
15. N. S. Astakhina and V. G. Gurevich, Ukr. J. Chem. **36**, 886 (1970).
16. Y. Marcus, J. Phys. Chem. **62**, 1314 (1958).

17. J. A. Goldman, J. Electroanal. Chem. **16**, 47 (1968).
18. J. J. Lingane, Electroanalytical Chemistry (Interscience, New York, 1958), 2nd Ed., pp. 139-141.
19. C. E. Hedrick, in Annual Progress Report for the Period July 1968 to June 1969, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-250, pp. 16-19.
20. T. Anfält and D. Jagner, Anal. Chim. Acta **57**, 165 (1971).
21. J. W. Frazer, A. M. Kray, W. Selig, and R. Lim, Anal. Chem. **47**, 869 (1975).
22. J. E. Harrar and E. Behrin, Anal. Chem. **39**, 1230 (1967).
23. S. B. Brummer, J. I. Ford, and M. J. Turner, J. Phys. Chem. **69**, 3424 (1965).
24. J. Bravacos, M. Bonnemay, E. Levart, A. Pilla, C. R. Acad. Sci. Paris **C265**, 337 (1967).
25. K. Klinedinst, J. A. S. Bett, J. MacDonald, and P. Stonehart, J. Electroanal. Chem. **57**, 281 (1974).
26. L. Z. Bodnar and M. W. Lerner, in Annual Progress Report for the Period July 1973 through June 1974, U.S. Atomic Energy Commission, New Brunswick Laboratory, N.J., Rept. NBL-272 (1974), pp. 13-25.

Appendix: Procedure for Testing VOSO_4 Solution for Vanadium(V) by Controlled-Potential Coulometry

Equipment: 1. Controlled-potential coulometry system

2. Electrolysis cell with platinum-gauze working electrode

Reagents: 1.5 M H_3PO_4

0.1 M H_2SO_4

Standard vanadium(V) solution; ~1 mg vanadium/ cm^3 (optional)

Procedure: A. Preparation of VOSO_4 Solution

1. Weigh out and place in a 100 cm^3 beaker 7.5 g of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ salt.
2. Place a magnetic stirring bar in the beaker, then add from a graduated cylinder 50 cm^3 of 0.1 M H_2SO_4 .
3. Stir the solution 5 to 10 minutes until the salt has dissolved.

B. Pretreatment of Platinum Electrode

1. Soak the electrode for 1 h in 50% HNO_3 , prepared fresh so it is warm at the start of pretreatment. Rinse with water. Immerse the electrode in hot, concentrated HCl , then allow to soak in the cooling acid for 1 h. Rinse with water.
2. Allow the electrode to soak in water overnight before using.

C. Coulometric Analysis Procedure

1. Fill both reference and counter-electrode compartments of the cell with 1.5 M H_3PO_4 .
2. Before coulometric measurement, deoxygenate solutions with inert gas for seven minutes.

3. Carry out several blank determinations with cell solution consisting of 10 cm³ of H₂O and 15 cm³ of 1.5 M H₃PO₄. Deoxygenate the solution thoroughly, and electrolyze the solution for 10 minutes at +0.40 V vs SCE. Repeat blank runs until the background current is below 25 µA and the blank is less than 0.015 mg of vanadium.
 4. Determine the quantity of vanadium(V) in 10 cm³ of VOSO₄ solution prepared as described above, by addition of VOSO₄ solution to 15 cm³ of 1.5 M H₃PO₄ in the cell, deoxygenation of the cell solution, and reduction as in Step C3.
 5. Correct the measurements of the VOSO₄ solution for the blank value determined in Step C3.
 6. The net quantity of vanadium(V) found in the coulometric determination, multiplied by 1.3, gives the equivalent quantity of uranium that would be oxidized by the vanadium(V) in 160 cm³ of diluent made with this sample of VOSO₄·2H₂O. This must be less than 0.05 mg uranium.
- D. Standard Addition Determination of Vanadium(V) (Optional)
1. After determination of vanadium(V) in the VOSO₄ solution in Step C4, switch the potentiostat to standby. Do not rinse out the cell solution.
 2. Add to the cell solution 0.1 cm³ of a solution containing ~1 mg vanadium(V) prepared as described below.
 3. Continue deoxygenating the solution for 3 minutes, then electrolyze the solution at +0.40 V for 10 minutes or until the current decreases to 25 µA. The readout should indicate ~100 µg of vanadium, and 90 to 95% of the quantity of vanadium(V) added should be recovered.
 4. Correct the quantity of vanadium(V) found in the VOSO₄·2H₂O for the quantity of added standard vanadium(V) found.

E. Preparation of Standard Vanadium(V) Solution

1. Weigh out and place in a 250 cm³ Erlenmeyer flask ~0.1 g of high-purity vanadium wire.
2. Add to the flask 5 cm³ concentrated HNO₃ and 5 cm³ concentrated H₂SO₄. Heat on a hot plate until dissolution of the metal is complete. If necessary, add a few cm³ more of concentrated HNO₃. Heat strongly for 30 minutes after dissolution is complete.
3. Cool the solution to room temperature, add 10 cm³ H₂O, mix, then add 2 g ammonium persulfate (NH₄)₂S₂O₈, mix, and heat again on the hot plate.
4. Bring the solution to a gentle boil for at least 15 minutes to ensure that all of the vanadium has been oxidized to vanadium(V) and the excess persulfate has been destroyed.
5. Transfer the solution to a 100 cm³ volumetric flask and dilute to volume with H₂O.
6. Verify the concentration of the vanadium standard solution by coulometric determination as described in C, taking 1 cm³ aliquots of the standard solution and electrolyzing at +0.55 V vs SCE.¹¹

- Notes:
1. The use of H₃PO₄ supporting electrolyte ensures that moderate amounts of impurity iron(III) will not interfere.
 2. The large excess of vanadium(IV) compared to the vanadium(V) requires the use of a more negative potential for the VO₂⁺ solution than that recommended in Ref. 11 for relatively pure vanadium(V) solutions. Even so, complete recovery in the standard addition procedure is still not attained. So a correction for this must be applied.