

RECORDS ADMINISTRATION



ACSY

ACC# 732227
DP-MS-68-68

COULOMETRIC TITRATION OF MICROGRAM AMOUNTS OF
AMERICIUM AT THE CONDUCTING GLASS ELECTRODE

by

R. C. Propst

SRL COPY

Proposed for publication

in

Analytical Chemistry

This document was prepared in conjunction with work accomplished under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of 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. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900, email: orders@ntis.fedworld.gov online ordering: <http://www.ntis.gov/ordering.htm>

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865) 576-8401, fax: (865) 576-5728, email: reports@adonis.osti.gov

COULOMETRIC TITRATION OF MICROGRAM AMOUNTS OF
AMERICIUM AT THE CONDUCTING GLASS ELECTRODE

by

R. C. Propst

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina 29801

ABSTRACT

Coulograms of Am(III) in carbonate electrolyte exhibit a well-defined wave for the Am(III)-Am(V) oxidation step at the conducting glass electrode. This wave provides the basis of a method for the quantitative titration of this element at the 30-microgram level with a precision of 1.5%. The method is restricted to pure solutions; corrections are required for the partial oxidation of Am(V) to Am(VI) and the reduction of Am(VI) by water.

INTRODUCTION

Americium, a by-product in nuclear fuel processing, is an important intermediate in the production of the higher actinides by reactor irradiation. The principal isotope is ^{243}Am which decays by alpha emission with a half-life of 7370 ± 40 years(1). A direct coulometric method for americium based on the stability of Am(III) and Am(V) in carbonate media was developed for the half-life study, and was suitable for calibration of aliquots containing 20-30 μg of americium; however, attempts to analyze larger samples (50 μg) with improved precision needed in accountability analysis gave high results. A thorough study of the electrochemistry of americium at the conducting glass electrode was undertaken to determine the cause of the bias.

From published reports, the oxidation of Am(V) to Am(VI) and the instability of Am(VI) in aqueous solution were plausible interfering reactions. In aqueous solutions, americium is normally trivalent. Because oxidation of Am^{3+} to AmO_2^+ involves the formation of oxygen bridges, the reaction is irreversible; however, once the AmO_2^+ ion is formed, the Am(V)-Am(VI) couple can be used to determine this element coulometrically. Koehly(2) was the first to describe a coulometric method for americium. He oxidized americium to Am(VI) by exhaustive electrolysis at the platinum electrode, and determined the americium by coulometrically reducing Am(VI) to Am(V). This method requires

excessively long electrolysis times (several hours) to quantitatively oxidize the americium. Stokely(3) shortened the procedure by replacing the electrolysis with a chemical oxidation. These authors also investigated the loss of Am(VI) due to reduction by water.

EXPERIMENTAL

Reagents

The ^{243}Am stock solution was purified by ion exchange, solvent extraction, and finally by the method of Moore(4). Alpha pulse height analysis of the product showed it to be 98.8 alpha per cent ^{243}Am with less than 0.05 alpha per cent ^{244}Cm . The ^{243}Am solution was standardized at 1.49 mg Am/ml by alpha pulse analysis and precision alpha counting in combination with mass spectrometry(1).

The isotopic purity of the ^{241}Am solution was confirmed by mass spectrometry.

All other solutions were prepared from reagent grade chemicals and demineralized laboratory distilled water.

During titration, the solutions were purged continuously with helium that had been bubbled through distilled water.

Equipment

The scanning coulometer with automatic scan rate control has been described(5); both the controlled-potential and scanning modes were used. All titrations were initiated at the equilibrium potential of the working electrode with respect to the solution. For electrolysis at controlled-potential, the potential was advanced manually from the equilibrium potential to the desired electrolysis potential. This precaution prevented amplifier overload.

The titration cell assembly (Figure 1), was similar to those previously described(6) except for the conducting glass electrode (CGE)(7) which consisted of a layer of antimony-doped, tin oxide on the inner surface of the titration cell. A platinum wire sealed through the side of the cell made ohmic contact with the conducting coating. All potentials were measured with respect to the mercury: mercurous sulfate (1M H_2SO_4) reference electrode (MSE). The MSE had a potential of 0.420 V (includes junction potentials) versus the saturated calomel electrode in 0.1M LiClO_4 - 0.05M Na_2CO_3 .

The CGE's were fabricated from borosilicate glass. To assure positive contact between the platinum wire and the tin oxide coating, the inner platinum connection was spotted with Liquid Bright Platinum (Engelhard Industries, East Newark, N. J.). This coating was air dried and fired at 650°C. The

tin oxide coating was applied by heating the cell to 600°C and spraying the inside surface with a solution that was 2.8 M in stannic chloride, 0.04M in antimony trichloride, and 1.2M in hydrochloric acid(8). A DeVilbiss #40 Nebulizer (DeVilbiss Co., Somerset, Pennsylvania) was used for spraying. The air pressure was 5 psig, and the spraying time was two minutes.

The cell resistance was measured by substituting an equivalent volume of mercury (10 ml) for the sample solution, and recording current-voltage curves between a tungsten contact immersed in the mercury and the platinum connection to the conducting coating. The scan rate was 5 volts per minute. The current-voltage curves were linear, and resistances for typical cells varied from 14 to 40 ohms.

The completed cells were evaluated by recording cyclic voltammetric and chronopotentiometric curves for the ferrocyanide-ferricyanide couple in 0.16M potassium chloride. The results were in complete agreement with the findings of Kuwana(7), which indicated that these electrodes would be suitable for electrochemical studies.

Procedure

The general titration procedure has been described(5), double-layer compensation was used, but residual current compensation was not required. The capacitance of the electrical double-layer at the CGE in 0.1M LiClO₄ - 0.05M Na₂CO₃ was estimated to be 130 μ fd/cm².

In this study, the electrolyte was preoxidized and reduced and background scans were recorded to assure that no americium remained in the cell from previous titrations. Carryover of electroactive contaminants from previous titrations was minimized by oxidizing the americium before discarding the solution. The cell was filled with 1M nitric acid when not in use.

Because cell resistance was low (<40 ohms) and the electrolysis currents were small (<30 μ a), the coulograms were not corrected for the voltage drop introduced by the surface resistance of the CGE.

RESULTS AND DISCUSSION

Titration Behavior

Typical coulograms showing the titration behavior of americium in carbonate electrolyte at the CGE are shown in Figure 2. The useful pH range for the titration was 10.0 to 11.5. Below pH 10.0, the wave at +0.26 V shifted in the anodic direction and merged with the wave corresponding to the anodic limit for the solvent-electrolyte system. Above pH 12.0, no oxidation of Am(III) was observed. The wave near -0.04 V always appeared on the reduction scan when the previous oxidation scan extended into the region more positive than +0.45 V. Since high carbonate concentrations (>0.05 M) appeared to favor the production of the species responsible for the wave at -0.04 V, an electrolyte of 0.1M LiClO_4 - 0.05M Na_2CO_3 was selected to minimize this effect.

Am(III) - Am(V) Couple

The wave at +0.26 V was assigned to the oxidation of Am(III) to Am(V); the wave at -0.77 V was assigned to the reduction of Am(V) to Am(III). These assignments were based on Am^{3+} as the stable species in aqueous solution, a two-electron change for the oxidation and reduction steps and the irreversible behavior of the system.

Because the higher valence states of americium are known to be unstable in aqueous solution, the americium stock solution was assumed to contain only the Am^{3+} species. This assumption was supported by coulograms for the reduction of aliquots of the stock solution which essentially duplicated background scans.

The number of electrons involved in the oxidation - reduction steps at +0.26 V and -0.77 V was determined by titrating aliquots of the isotopically pure solution of ^{241}Am . The ^{241}Am solution was utilized here since the half-life has been determined accurately by calorimetry(9), and the solution could thus be standardized precisely by alpha counting. Although the results were consistent with a two-electron transfer for both the oxidation and reduction steps, the number of electrons calculated from the height of the oxidation wave was always slightly more than two. This behavior was later attributed to a partial oxidation of Am(V) to Am(VI) as will be explained.

The irreversible behavior of the Am(III)-Am(V) couple (as anticipated from the chemistry of the system) was evidenced in the wide separation between the oxidation and reduction waves and by the agreement between the observed and theoretical response of the instrument to an irreversible process.

The coulometer records well defined waves for an irreversible process due to a unique method of scan rate control in which the instrument maintains the product of the electrolysis current (i) and the scan rate (dE/dt) at a constant value. Thus the slope of the recorded coulogram is given by,

$$\frac{dQ}{dt} = \frac{-i^2}{a}$$

where a = scan rate constant, 10^{-9} volt amp sec $^{-1}$. Although this equation could not be solved in closed form for a coulometrically reversible process, a solution was obtained for an irreversible process in which the rate for the backward reaction was negligible ($k_{s,h} \leq 10^{-5}$ cm sec $^{-1}$). The following solution for the reduction of a species that is initially in the oxidized form was based on diffusion layer theory for coulometric processes in stirred solution(10).

$$\frac{Q_c}{Q_t(Q_t - Q_c)} = \frac{\beta^2 RT}{a\alpha nF} \left[\frac{D_o}{D_o + k_{s,h} \delta_o \exp -\alpha\theta} - \frac{D_o}{D_o + k_{s,h} \delta_o} + \ln \left(\frac{D_o + k_{s,h} \delta_o \exp -\alpha\theta}{D_o + k_{s,h} \delta_o} \right) \right]$$

$$\text{where } \theta = \frac{nf}{Rt} (E - E_c^\circ)$$

E_c° = potential for $i = 0$, identified with standard potential(10).

E = electrolysis potential

Q_t = theoretical height of reduction wave, coulombs

Q_c = height of reduction wave at E , coulombs

$$\beta = AD_o / \delta_o V$$

A = electrode area, cm^2

D_o = diffusion coefficient, $\text{cm}^2 \text{ sec}^{-1}$

δ_o = Nernst diffusion layer thickness, cm

$k_{s,h}$ = heterogeneous rate constant, cm sec^{-1}

V = volume of solution, cm^3

and the remaining symbols have their unusual significance. The corresponding equation for the oxidation process was identical except that $-\alpha$ was replaced by $(1-\alpha)$,

D_o by D_r , δ_o by δ_r , and Q_c by Q_a .

Before the theoretical coulograms could be calculated, β had to be determined by controlled-potential coulometry, and $k_{s,h}$, E_c° , and α had to be estimated from the coulograms. Thus

current-time curves were recorded at controlled potential in the limiting current region for both the oxidation and reduction steps. In each case, graphs of $\log i$ versus t were convex upward, indicating that the electrode reactions were more complex than could be explained in terms of simple irreversible theory. Similar phenomena have been reported for vanadium solutions by Israel and Meites(11).

Because of this complex behavior, only estimated values for β , $k_{s,h}$, E_c° and α could be obtained from the data; coulograms were calculated from these estimated values. The results (Figure 2) show that the theoretical coulograms are in qualitative agreement with the observed response.

Further evidence to support the above findings concerning the irreversible nature of the Am(III) - Am(V) couple was obtained in experiments in which the Am(III) solution was electrolyzed to produce calculated amounts of Am(V). Following the electrolysis, attempts were made to record the equilibrium potentials for the various Am(III): Am(V) ratios under zero current conditions. In every instance, the potentials were so unstable that no steady state values could be obtained.

Because of the better definition of the oxidation step, this wave was preferred for the quantitative determination of americium. Therefore, the factors responsible for the increased height of this wave were investigated.

Am(V) Oxidation

Two explanations for the increased height of the Am(III)-Am(V) wave were considered. The first, the formation of Am(III) via disproportionation of Am(V) proved to be negligible. The second, a one-electron oxidation of Am(V) by a coulometric process, proved to be responsible for the increased height of the Am(III)-Am(V) wave.

The disproportionation of Am(V) was studied by coulometrically oxidizing Am(III) to Am(V), allowing the Am(V) solution to stand for periods of 1 hour, and then scanning the region from 0.0 to +0.45 V to determine the amount of Am(III) formed by disproportionation. In no case was the presence of Am(III) detected in the Am(V) solutions.

The coulometric oxidation of Am(V) was established by controlled-potential coulometry. Reduction coulograms of americium solutions that had been exhaustively electrolyzed at 0.55 V indicated that the height of the unidentified wave at -0.04 V approached one-half that of the waves assigned to the Am(III) - Am(V) couple. Thus the wave at -0.04 V was tentatively assigned to the one electron reduction of Am(VI). To identify the mechanism responsible for the formation of Am(VI), the electrolyte solution containing 29.8 μg of ^{243}Am was exhaustively electrolyzed at controlled-potential (+0.4 V) to oxidize Am(III) to Am(V) and Am(VI). Immediately following the

oxidation, the solution was reduced at -0.36 V to reduce the Am(VI) to Am(V). The oxidation procedure was repeated in 30 -mV increments from +0.4 to +0.55 V. The amount of Am(VI) produced at each potential was calculated from the integrated current at -0.36 V and corrected for background processes(12) and for the reduction of Am(VI) by water. The corrected results gave a Nernst plot with a value of 0.065 for RT/F and a half-wave potential of +0.44 V. Although these results indicate that the oxidation of Am(V) to Am(VI) was a coulometrically reversible process, the irreversible nature of the reduction process as evidenced by the potential for the Am(VI)-Am(V) wave cannot be explained at this time.

Reduction of Am(VI) by Water

During studies of the Am(V) oxidation process, Am(VI) solutions were observed to decompose slowly on standing; with a rate of decomposition that was greater than could be explained on the basis of self-reduction via radiolysis. Stokely and Shultz(3) attribute the loss to the reduction of Am(VI) by water by a process that is first order with respect to the Am(VI) concentration. This reaction was investigated because results for the amount of Am(VI) in solution determined by controlled-potential reduction must be corrected for the reduction of Am(VI) by water.

If the loss of Am(VI) via reduction by water is first order in terms of the Am(VI) concentration, then the change in Am(VI) concentration during controlled-potential reduction is given by,

$$\frac{d \text{Am(VI)}}{dt} = - k \text{Am(VI)} - \beta \text{Am(VI)} \quad (1)$$

where Am(VI) = amount of Am(VI) in solution after time = t

k = rate constant for the reduction of Am(VI) by
water

β = rate constant for coulometric reduction of Am(VI)

Integrating the above equation gives

$$\text{Am(VI)} = \text{Am}_t \exp - (\beta + k)t \quad (2)$$

where Am_t = amount of Am(VI) at t = 0.

Since the rate for the coulometric production of Am(V) is given by,

$$\frac{d \text{Am(V)}_e}{dt} = \beta \text{Am(VI)} \quad (3)$$

substitution for the bulk concentration of Am(VI), (2), into (3) and integrating gives,

$$\text{Am(V)}_e = \frac{\beta}{\beta + k} \text{Am}_t [1 - \exp - (\beta + k)t] \quad (4)$$

where Am(V)_e = amount of Am(V) produced by coulometric reduction of Am(VI).

For long electrolysis times, Equation 4 reduces to,

$$\text{Am(V)}_e = \frac{\beta}{\beta + k} \text{Am}_t \quad (5)$$

The ratio $\beta/(\beta+k)$ was obtained by exhaustively electrolyzing known amounts of americium at +0.56 V to produce Am(VI). The solutions were then reduced immediately at -0.36 V and the amounts of Am(V)_e calculated from the integrated current. The oxidation step was assumed to give essentially complete conversion of the americium to Am(VI). This assumption was justified on the basis of a small value for k as will be seen. Values for β and k were obtained in a like manner except that the Am(VI) solutions were allowed to stand for periods of up to one hour before the reduction titration was begun. The Am(VI) remaining in the solutions after known periods were calculated by Equation 5, and k was determined from the following equation for the reduction of Am(VI) by water.

$$\text{Am(VI)} = \text{Am}_t \exp - kt \quad (6)$$

where Am(VI) = amount of Am(VI) remaining after standing for time = t

Average values for β , k , and $\beta/(\beta+k)$ were $5.0 \times 10^{-3} \text{ sec}^{-1}$, $2.2 \times 10^{-4} \text{ sec}^{-1}$, and 0.95 respectively.

Am(VI) Correction

The amount of Am(VI) produced in recording a coulogram of the Am(III)-Am(V) wave is a function of the amount of americium in solution and the anodic potential limit for the scan. To correct the Am(III)-Am(V) wave for the amount of Am(VI) produced, a correction curve was prepared as follows:

The potential at which the wave height corresponded to 99.5% conversion of Am(III) to Am(V) was estimated from the equation for the coulometric wave by assuming that $n = 2$, $(1 - \alpha) = 0.9$, $Q_t = 0.1$ coulombs and that the apparent half-wave potential occurred where $Q_a = Q_t/2$. The remaining parameters are given on Figure 2. The result of +0.40 V was consistent with that obtained for a Nernst plot of the data from a coulogram of the Am(III)-Am(V) wave. Thus solutions containing from 7.4 to 59.6 μg of americium were scanned to +0.4 V and the amounts of Am(VI) thus produced determined by reduction at controlled-potential at -0.36 V. When corrected for a blank titration and for the reduction of Am(VI) by water the results were conveniently expressed by the following equation.

$$\text{Correction, mQ} = 0.3 + \log (.024H - 1.15)$$

where H = observed wave height at +0.4 V, millicoulombs

This equation was used to correct the analytical data for the amounts of Am(VI) produced in recording the coulogram for the Am(III)-Am(V) oxidation.

Analytical Results

The results for the coulometric titration of ^{243}Am are given in Table I. The amount of ^{243}Am taken was calculated from the half-life for $^{243}\text{Am}(1)$; the results are included for comparison purposes. The amount of ^{243}Am found was calculated from the height of the wave at +0.40 as corrected for the amount of Am(VI) produced. The standard deviation for the method was calculated by the method of least squares. The intercept of the least-squares curve was not statistically significant at the $P = 0.02$ level. The slope of the least-squares curve indicated an average value of 1.48 mg $^{243}\text{Am}/\text{ml}$ for the stock solution. This compares favorably with the value of 1.49 mg $^{243}\text{Am}/\text{ml}$ determined by radiochemical methods. The precision of the method at the 30- μg level was 1.5%.

Interferences

A limited study of the effect of diverse ions indicated that purification will be necessary if this technique is to be used with other than pure solutions.

Neither chloride nor nitrate interferes at 0.01M concentrations. However, sulfate and flouride must be avoided. Sulfate produces an anodic shift of the Am(III)-Am(V) wave, and flouride damages glass surfaces.

Most cations interfere; plutonium, neptunium, uranium, and ruthenium undergo redox reactions near the Am(III)-Am(V) wave. Iron precipitates and scavenges some of the americium. Curium and other radioelements interfere because radiolysis products contribute to the background processes.

Acknowledgments

The author is indebted to Dr. L. C. Brown and Dr. H. P. Holcomb who provided the ^{241}Am and ^{243}Am solutions respectively, and to D. A. Brown for counting data. The cooperation of R. H. Searle in preparing the CGE is acknowledged.

The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

REFERENCES

1. L. C. Brown and R. C. Propst, accepted for publication in *J. Inorg. and Nucl. Chem.*
2. G. Koehly, *Anal. Chim. Acta.*, 33, 418 (1965).
3. J. R. Stokely and W. D. Shultz, Paper presented at the Eleventh Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn. Oct. 10-12, 1967.
4. F. L. Moore, *Anal. Chem.*, 35, 715 (1963).
5. R. C. Propst, *Anal. Chem.*, 35, 958 (1963).
6. R. C. Propst, *Anal. Chem.*, 40, 244 (1968).
7. T. Kuwana, R. K. Darlington, and D. W. Leedy, *Anal. Chem.*, 36, 2023 (1964).
8. J. M. Mochel (to Corning Glass Works), U. S. Patent 2,564,707 (Aug. 21, 1951).
9. F. L. Oetting and S. R. Gunn, *J. Inorg. Nucl. Chem.*, 29, 2659 (1967).
10. P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, 1954, Chapter 9.
11. Y. Israel and L. Meites, *J. Electro Anal. Chem.*, 8, 99 (1964).
12. L. Meites and S. A. Moros, *Anal. Chem.*, 31, 23 (1959).

TABLE I

Coulometric Determination of Americium

Sample: 1/10 dilution of ^{243}Am solution.

<u>Sample Size</u> <u>μl</u>	<u>No. of</u> <u>Titration</u> s	<u>Am taken,</u> <u>μg</u>	<u>Am Found</u>	
			<u>$\mu\text{g}(\text{ave})$</u>	<u>$\mu\text{g}/\text{ml}(\text{ave})$</u>
50	4	7.5	7.4	148
100	4	14.9	14.9	149
150	3	22.4	22.6	150
200	5	29.8	30.0	149
250	2	37.3	37.1	148
300	1	44.7	44.0	147
400	1	59.6	59.2	148
			$\sigma = 0.46 \mu\text{g}$	148

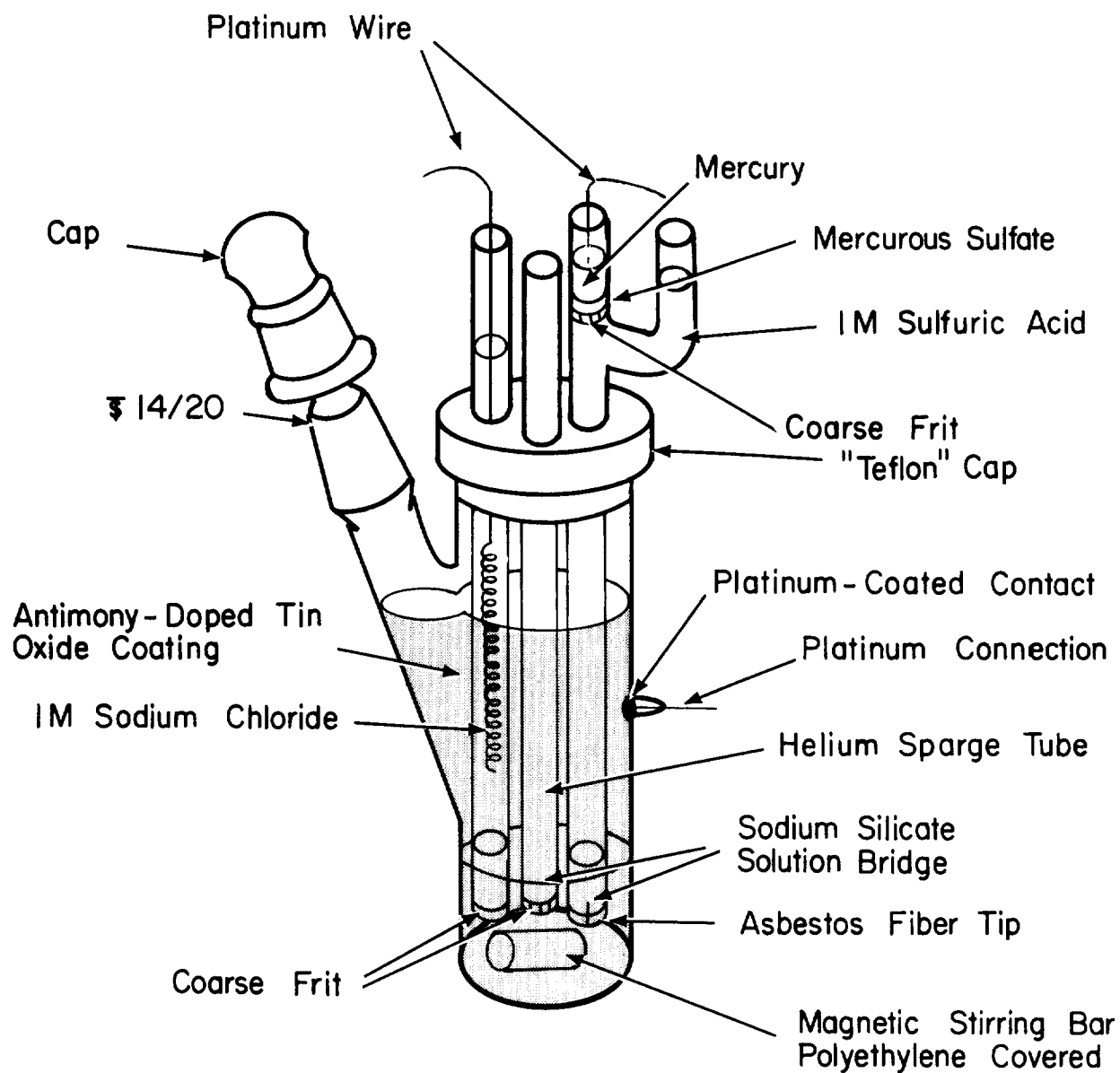


FIG. 1 TITRATION CELL ASSEMBLY

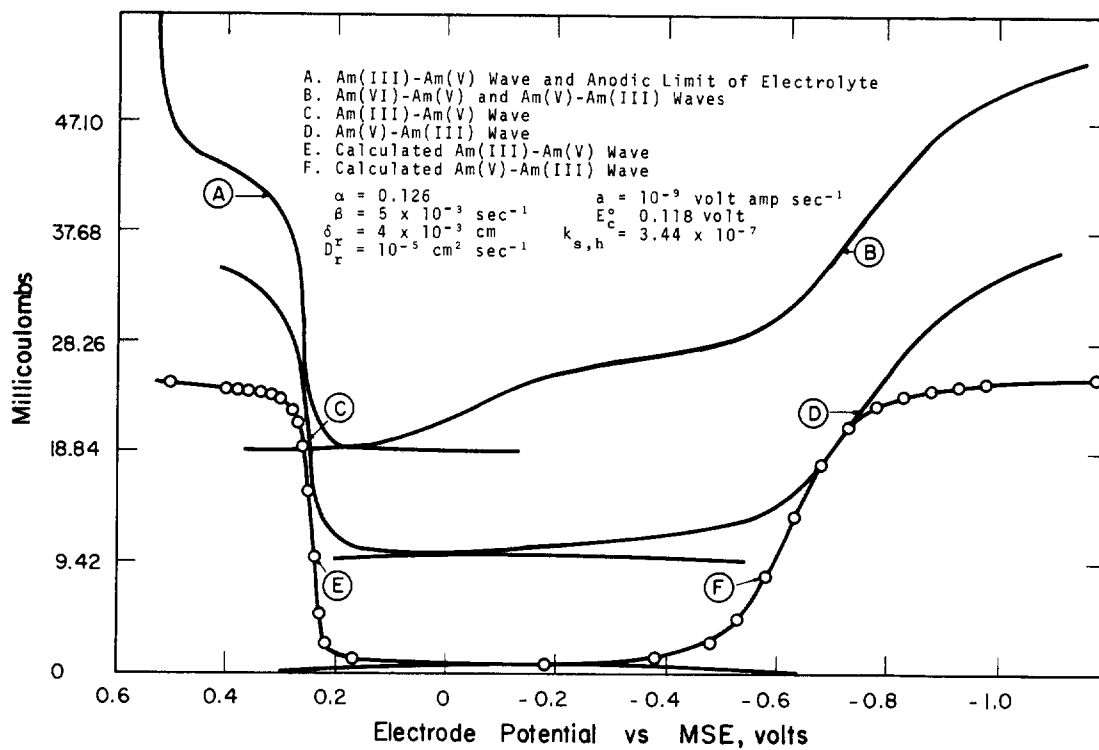


FIG. 2 COULOGRAMS OF 29.8 μg ^{243}Am IN 0.1 M LiClO_4 - 0.05 M Na_2CO_3