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COULOMETRIC TITRATION OF CHLORIDE AND OF CHROMIUM IN HOMOGENEOUS REACTOR TYPE SOLUTIONS

W. D. Shults, II
P. F. Thomason

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COULOMETRIC TITRATION OF CHLORIDE AND OF CHROMIUM IN HOMOGENEOUS REACTOR TYPE SOLUTIONS

W. D. Shults, II, and P. F. Thomason

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ABSTRACT

This report describes the modifications to and extension of two existing coulometric titration methods so that microgram quantities of chloride and of chromium can be determined in Homogeneous Reactor type solutions.

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I. Introduction

Coulometric titration is a relatively new method of analysis which is especially suited to the determination of very small (microgram and submilligram) quantities of substances. Because of the relatively few manipulations required in a coulometric titration, the method should be extremely useful for the analysis of radioactive solutions. This report describes coulometric titration methods for the determination of chloride and of chromium which have been developed for use in the analysis of Homogeneous Reactor (HR) type solutions.

Each of these titrations has been reported previously[1,2] for the determination of milligram and submilligram quantities of chloride and of chromium(VI). The modifications necessary to make these methods suitable for the determination of microgram quantities of these ions in HR type solutions are discussed, the results of analyses made by them are given, and the procedures are appended to this report.

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II. Summary

This report describes the modification and extension of existing coulometric titration methods for the determination of chloride and of chromium(VI) to the analysis of HR type solutions for these ions.

The coulometric titration of chloride has been reported by Lingane.[2] He titrated chloride with silver ions that were electrolytically generated with constant current from a silver wire immersed directly in the test solution. By titration in a cold "electrolyte" solution that contained approximately 50 % methanol and by maintenance of a small (3 to 6 ml) total volume of solution, Lingane's method has been extended to the determination of as little as 4 µg of chloride (contained in 0.1 to 3 ml of solution); the relative standard deviation of the data was 4.5 %. The interference of chromate ions can be eliminated by reduction to chromium(III) before the titration is made.

Similarly, the coulometric titration of chromium has been reported by Cooke and Furman.[1] They titrated chromium(VI) with iron(II) that was formed by electrolytic reduction of iron(III) with constant current at a platinum cathode immersed directly in the solution. By the maintenance of a small (4 to 7 ml) total volume of solution and by use of a pair of polarized platinum wires as the indicating electrode system, their method has been extended to the determination of as little as 4 µg of chromium(VI) (contained in 0.1 to 3 ml of sample solution); the relative standard deviation of the data was 2.5 %. The relative standard deviation was 1.0 % when 10 to 100 µg of chromium(VI) was titrated. The "electrolyte" solution in which titrations are made must be acidified with hydrochloric acid in order to prevent copper interference. Other constituents of HR type solutions do not interfere. A procedure for the preliminary oxidation of chromium(III) to chromium(VI) is included.

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III. General Discussion

A. Principles of Coulometric Titration

A coulometric titration is one in which the reagent that reacts stoichiometrically with the substance being determined is generated electrolytically. The quantity of the substance determined is computed (by Faraday's law) from the coulombs of current required to complete the reaction rather than from the volume of a standard titrant, as is the case in a volumetric titration. By generation of the titrant with constant known current, the quantity of electricity required can be determined simply by timing the electrolysis. The titrant must be generated with 100 % current efficiency and must react stoichiometrically, and preferably rapidly, with the substance being titrated. End points can usually be detected by the methods employed in ordinary titrations.

The titrant is frequently generated at an electrode that is immersed directly in the test solution. For example, silver ions can be electrolytically generated with 100 % current efficiency from a pure silver wire immersed directly in the test solution; this forms the basis for the coulometric titration of chloride ions. As the silver ions are formed, they react with any chloride ions present to form insoluble silver chloride according to the equation

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow \ .$$

This reaction proceeds until the chloride ions are exhausted, at which time silver ions begin to be present in excess. The presence of excess silver ions

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causes an increase in the potential of the solution, as indicated by a silver wire vs S.C.E. system, thereby signalling the end point.

Similarly, chromium(VI) can be determined by reaction with iron(II) which is furnished by electrolytic reduction (at 100 % current efficiency) of iron(III) at a platinum cathode immersed in the solution. Dichromate ions are reduced to chromium(III) by iron(II) according to the equation.

$$Cr_2O_7^{=} + 6\ Fe^{++} + 14\ H^{+} \longrightarrow 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O.$$

This reaction proceeds until the chromium(VI) ions are exhausted at which time iron(II) begins to be present in excess. The presence of excess iron(II) causes an abrupt decrease in the potential of the solution, as indicated by the derivative polarographic method of end-point detection[3]. This potential change signals the end point.

Coulometric titration methods are especially suited to the determination of small quantities (submilligram and microgram) of substances since very small amounts of titrant can be added by means of small generating currents. Some other advantages of coulometric titration methods are (1) constancy of volume during the titration; (2) minimum of operational steps, (3) lack of necessity for standard solutions; (4) rapidity, accuracy, and precision; and (5) ease of automatization.

B. Automatic Coulometric Titrator

Coulometric titrations like those just described require the use of a power supply which furnishes and maintains a constant generating current. The automatic coulometric titrator (ACT) used in this work was developed by

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Stelzner et al.[4]. It electronically provides and maintains a constant (± 0.1 %) generating current which can be adjusted continuously to any value between zero and ten milliamperes. An ammeter is included in the circuitry and indicates approximately the current flowing. The exact value of the generating current is computed from Ohm's law by use of the measured potential drop across a standard 100-ohm resistor that is incorporated in the generating circuit.

This instrument, in conjunction with a Leeds and Northrup pH meter, also provides for automatic stoppage of the generating current at any preselected end-point potential between -1.4 and +1.4 volts. The potential of the solution is constantly monitored during the titration. When the potential, as indicated on the pH meter, reaches the value which has been preselected as the end-point potential, the titrator automatically stops the flow of generating current. Should the potential fall below the cutoff value, the flow of current will begin and continue until the cutoff potential is again attained. An electric timer is incorporated which measures the time of current-flow through the generating circuit.

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IV. Coulometric Titration of Chloride

A. Introduction

The coulometric titration of chloride has been reported by Lingane.[2] By the cooling and the decrease of the volume of the solution in which titrations are made, his method has been extended to the titration of 1-ml portions of solutions that contained 4 to 500 ppm of chloride. This method has been developed primarily for use in the analysis of HR type solutions but should be applicable to the determination of chloride in other solutions.

B. Discussion

1. The Method

Chloride ions react with silver ions which are generated electrolytically with constant current at a pure silver generating electrode immersed directly in the test solution. Insoluble silver chloride is formed according to the equation

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow \ .$$

The potential of the solution, i.e., the progress of the titration, is monitored by means of a silver wire vs S.C.E. system. The appearance of excess silver ions causes an increase in the potential of the solution and thereby automatically stops the timer and generating current. The end-point potential is taken as +0.230 volt vs S.C.E., and the amount of chloride titrated is calculated by Faraday's law from the known constant current used and the time required to titrate the sample to the end point. Lingane[2] titrated 0.5 to 5.0 mg of chloride in a

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total solution volume of approximately 50 ml by this method. He mentioned that the method might be applicable to the titration of smaller amounts of chloride if a smaller total volume of solution were used.

The coulometric titration of chloride ion with silver ion is improved when the solubility of silver chloride is decreased by cooling and by the addition of methanol to the solution being titrated. It was found that the coulometric titration of very small (4 to 400 μg) amounts of chloride can be conveniently made by use of a supporting "electrolyte" solution that contains the methanol. This solution is cooled and titrated to the end point, the sample is then added to it, and the solution is titrated back to the end point. By use of the same constant current in each of these titrations, errors caused by under- or overtitration are cancelled. The amount of chloride titrated is calculated from the known constant current used and the time required to titrate the sample back to the end point. This procedure also has the advantage that duplicate or triplicate portions of the same sample can be titrated consecutively in a single electrolyte solution because the solution is titrated back to the same end-point potential each time.

A total solution volume of 3 to 6 ml was used for the titration of 4 to 100 μg of chloride and consisted of 3 ml of "electrolyte" solution and 0.1 to 3 ml of sample solution. The potential change at the end point is reasonably rapid and is reproducible when 25 μg or more of chloride is titrated as just

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described. When less than 10 μg of chloride is titrated, the potential at the end point is somewhat sluggish in reaching equilibrium. In this case, increments of current must be added near the end point until enough silver ion is generated to maintain the solution potential at the end-point potential for a time interval of 1 1/2 minutes.

The automatic coulometric titrator used for these titrations automatically adds current until the end-point potential is reached, at which time it stops the flow of current. If the solution potential falls below that potential at which cutoff of current flow occurs, the flow of generating current begins again and continues until the end-point (cutoff) potential is again reached. Titration to a sluggish end point, such as is obtained with less than 10 micrograms of chloride, consists of a series of current additions, each addition being of shorter duration than the preceding one and the time between each addition gradually increasing. When the time between additions has increased to 1 1/2 minutes, the solution may be considered to be titrated to the end point.

When more than 100 μg of chloride is titrated, a total solution volume of 20 to 25 ml and a correspondingly larger silver generating electrode is used.

Any substance which reacts with silver or silver ion or which undergoes electrolytic reaction at the generating electrode will interfere in this titration. The only constituent of HR type solutions known to interfere is chromate, which forms slightly soluble Ag_2CrO_4 with silver ions. This interference can be eliminated by reducing $CrO_4^{=}$ to chromium(III) with hydroxylamine hydrosulfate ($NH_2OH \cdot H_2SO_4$) prior to the titration. However, the presence of chromium(III) was found to cause a slight rise in the potential of the

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"electrolyte" solution, so that it was necessary to titrate the sample to a slightly higher end-point potential than was necessary in the absence of chromium. The end-point corrections listed in Table 1 should be added to the usual end-point potential (+0.230 volt vs S.C.E.) when the corresponding amounts of chromium are present so that the sample is titrated to a corrected end-point potential.

A coating of AgCl gradually collects on the generating anode and can be removed by stirring a 1:4 NH_4OH solution around the anode. This treatment must be followed by three successive rinses of the anode with 0.5 N HNO_3.

2. The Apparatus

Titrations of less than 100 µg of chloride are carried out in a 15-ml weighing bottle (cell) which is fitted with a rubber stopper that supports two salt bridges and two silver wires. The generating system consists of a silver wire coil anode, mounted vertically inside the cell, and a platinum gauze cathode, immersed in a 3 % KNO_3—3 % HNO_3 solution which is connected to the test solution by means of one of the salt bridges. The indicating system consists of a silver wire indicator and a saturated calomel reference electrode which is connected to the test solution through the second salt bridge. The cell is jacketed with ice-water contained in a crystallizing dish; the test solution is stirred magnetically. A diagram of this apparatus and of the electrical hook-up is given in Fig. 1.

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Table 1

Results of Coulometric Titration of Chloride in Dilute Hydrochloric Acid Solutions

(The sample volume was 1 ml and the total solution volume was approximately 4 ml in each case. Final solution was approximately 60 % CH_3OH and 0.2 % HNO_3.)

Chromium Present,(a) µg	End-point Correction Applied, v	Analyses	Chloride, µg/ml Taken	Chloride, µg/ml Found(b)	Extreme Values from Average, %	S, %
---	---	15	82.8	82.2	± 1.2	0.9
---	---	16	20.6	20.6	± 4	2.4
---	---	15	4.1	4.2	± 6	3.7
5	+0.010	10	4.1	4.0	± 5	3.8
10	+0.015	6	4.1	4.1	± 6	3.5
50	+0.018	13	4.1	4.1	± 6	4.4
100	+0.018	11	4.1	4.1	± 5	3.0
250	+0.018	10	4.1	4.1	± 5	3.2

(a) Chromium present in sample as $K_2Cr_2O_7$.

(b) The average of N determinations.

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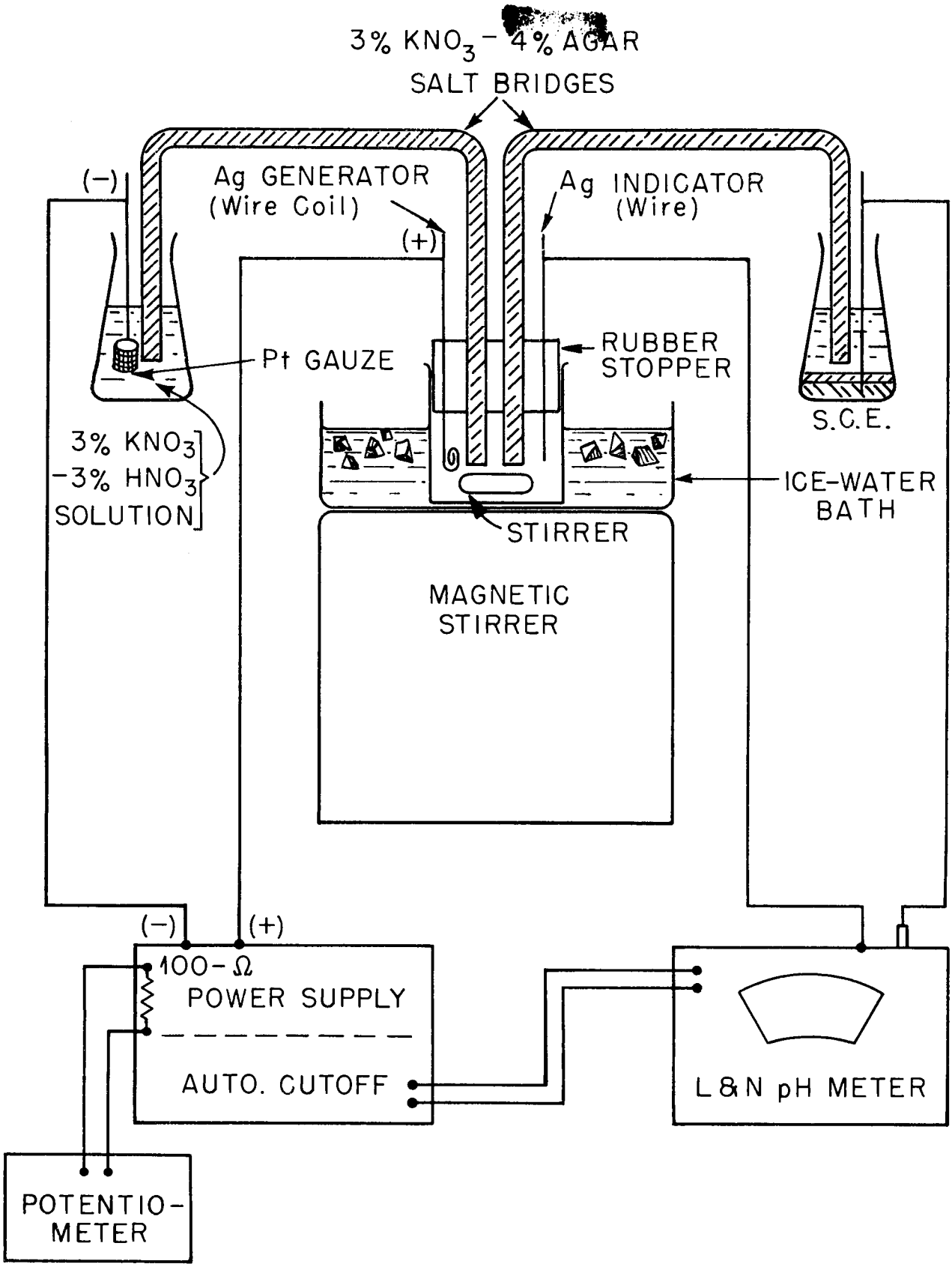

Fig. 1. Diagram of Apparatus and Instrument Setup for Coulometric Titration of Chloride.

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Titrations of more than 100 μg of chloride are made in a 50-ml beaker. The setup is similar to that described above except that a correspondingly larger silver wire coil is used as the generating electrode.

The automatic coulometric titrator developed by Stelzner et al.[4] furnishes the constant current required and also automatically stops the flow of current to the generating circuit when a preset end-point potential is reached. A clock is incorporated which measures the time during which current flows through the generating circuit.

C. Results

The results obtained by the titration of 1-ml aliquots of standard solutions of various chloride concentrations less than 100 μg/ml are listed in Table 1. The data in this table show that the coulometric titration method is well suited to the analysis of solutions that contain small amounts of chloride.

No precision data are given for samples that contained uranyl sulfate. However, several titrations were run on solutions that contained as much as 40 mg of U (as UO_2SO_4) per milliliter, and it was found that uranium has no adverse effect on the titration of chloride by this coulometric method.

D. Procedure

Sections IV, V, VI, and VII of Method No. 9 0822011, "Chloride in Homogeneous Reactor Type Solutions, Coulometric Titration Method", as written for tentative issue to the ORNL Master Analytical Manual are given in Apx. I.

Although the procedure was written specifically for use with the automatic coulometric titrator[4], the general procedure and principles will remain the same regardless of the instrumentation used.

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V. Coulometric Titration of Chromium

A. Introduction

The titration of milligram and submilligram quantities of chromium(VI) by means of electrolytically generated iron(II) has been reported.[1] This method has been modified so that microgram quantities of chromium(VI) can be titrated accurately and with good precision. Relatively large quantities of uranium and copper do not interfere; therefore the modified method should be useful for the analysis of HR type solutions.

B. Discussion

1. The Method

Chromium(VI) reacts with iron(II) which is generated electrolytically with constant current at a platinum (generating) cathode immersed in the test solution; chromium(VI) is reduced to chromium(III). The progress of the titration is monitored by means of a pair of polarized platinum wires immersed in the solution. The appearance of excess iron(II) causes an abrupt decrease in the indicated potential and thereby automatically stops the timer and the flow of generating current. Errors caused by the small amount of iron(II) required to depolarize the electrodes or by traces of iron(II) in the reagents are eliminated by pretitrating a quantity of chromium(VI) to the end point, adding the sample, and then titrating back to the end-point potential. The same constant current is used in each of these titrations and the time required to titrate the sample back to the end point is measured. Duplicate or triplicate aliquots of the same sample may be consecutively added to and titrated in the same "electrolyte" because the solution is titrated to the same end-point potential in each case.

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A relatively concentrated solution of ferric ammonium sulfate, acidified with H_2SO_4 and HCl, serves as the source of iron(II). Use of an HCl-acidified "electrolyte" solution greatly improves the sharpness of the potential change at the end point. The HCl also serves to eliminate the interference of copper which might be present in HR type solutions and to remove the Ag^+ catalyst used in the preliminary oxidation of the sample.

The use of a pair of polarized platinum wires as indicator electrodes[3] is necessary because other electrode systems -- platinum vs calomel and platinum vs tungsten -- were found to give poor end points in titrations of microgram quantities of chromium(VI). The platinum wires are polarized by means of a 45-v battery connected to them through a 20-Megohm resistor. Typical titration curves obtained by use of this indicator system are shown in Fig. 2. The potential change at the end point is rapid and reproducible.

Since each pair of electrodes will have a different surface area, it is necessary to establish the end-point potential by titrating two different quantities of chromium(VI) manually and plotting the titration curves as illustrated in Fig. 2. The potential at which the two curves intersect during the "break" is taken as the end-point potential for subsequent automatic titrations; its value was +0.230 v in the present work.

A minimum of care is required with this electrode system; the electrodes should be shorted together and immersed in distilled water when they are not in use.

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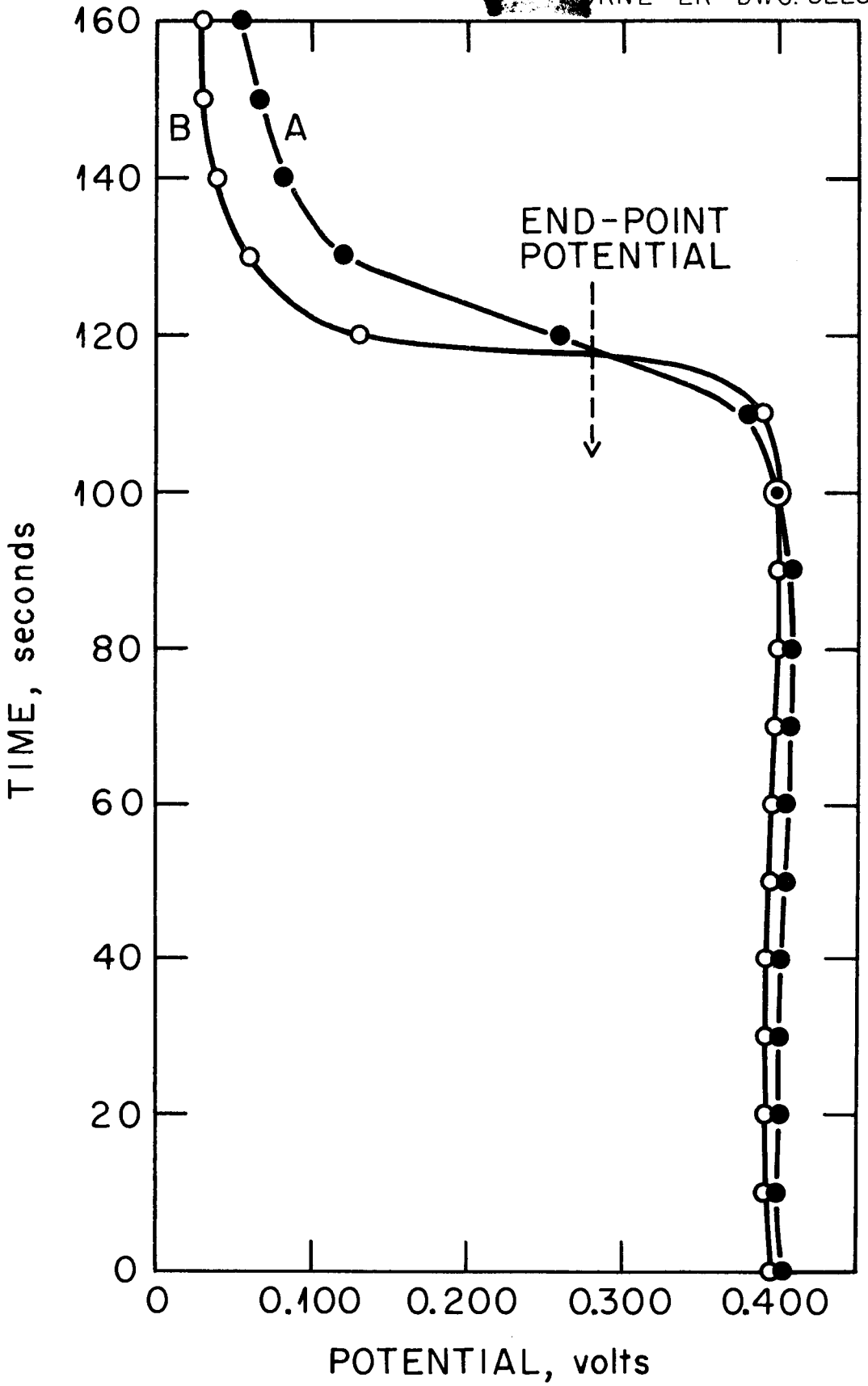

Fig. 2. Typical Titration Curves Obtained by Titration of Chromium (VI) with Electrolytically Generated Iron (II).

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Chromium(III) may be conveniently oxidized to chromium(VI) before titration by treatment with a solution of ammonium persulfate and a silver catalyst. The excess ammonium persulfate is destroyed by boiling the solution, and the Ag^+ catalyst is precipitated as AgCl upon addition of the sample to the "electrolyte" solution. The AgCl precipitate does not interfere with the titration.

Two other methods for the preliminary oxidation of chromium(III) to chromium(VI) were investigated: oxidation by hot concentrated perchloric acid and oxidation by treatment with sodium bismuthate. The perchloric acid treatment was found to be unsatisfactory for oxidation of microgram quantities of chromium. Treatment with sodium bismuthate accomplishes the oxidation but is not very satisfactory because a rather large dilution of the sample results from the filtration and washing steps that are necessary to obtain 100 % recovery of the chromium.

2. The Apparatus

A diagram of the instrument setup and apparatus for the coulometric titration of chromium(VI) is given in Fig. 3.

Titrations are carried out in a 15-ml weighing bottle (cell), which is fitted with a rubber stopper that supports a salt bridge and three electrodes. The generating electrode system consists of a 1 x 2 cm platinum "flag" cathode mounted vertically inside the cell and a platinum gauze anode immersed in a 3 %

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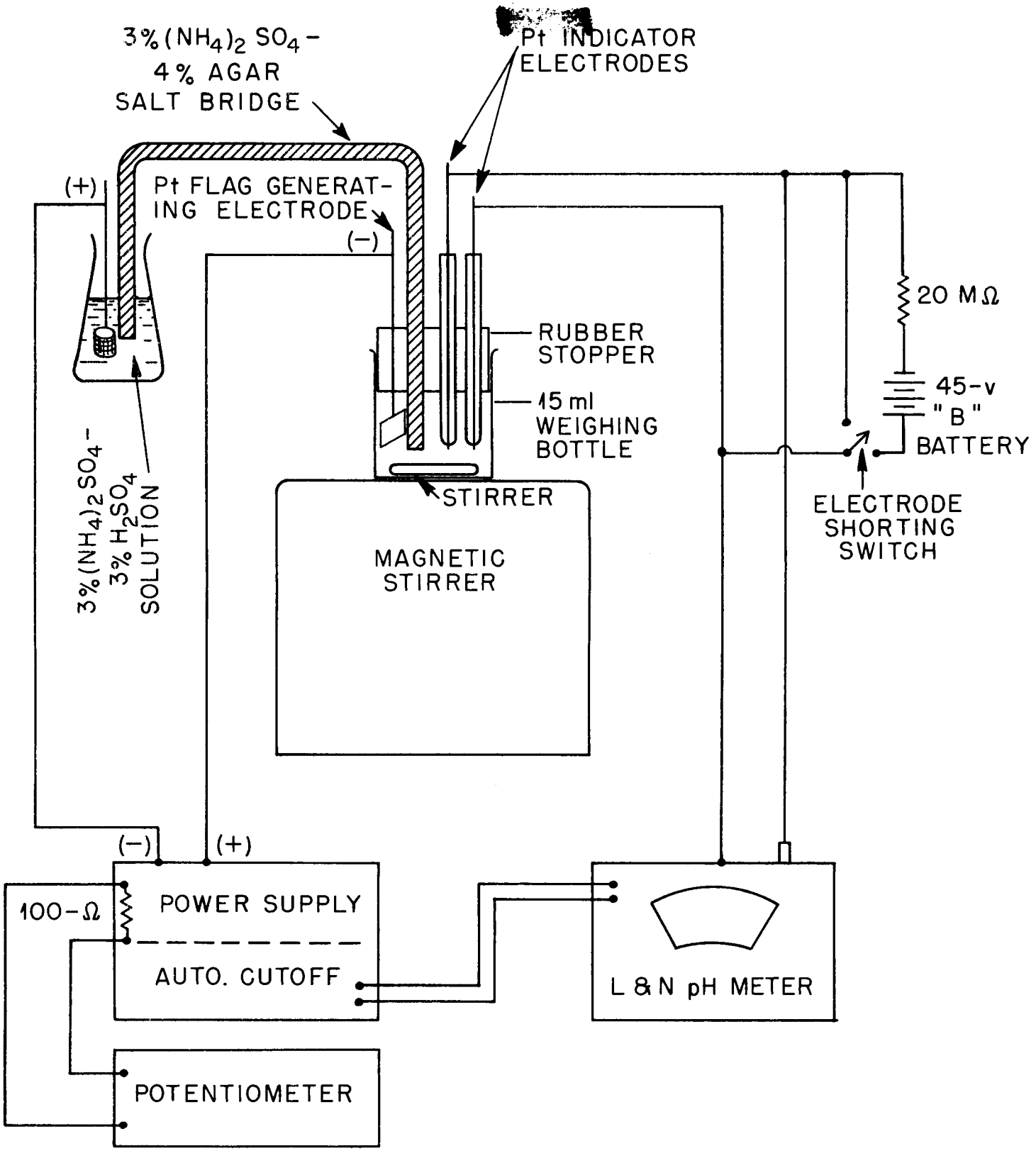

Fig. 3. Diagram of Apparatus and Instrument Setup for Coulometric Titration of Chromium(VI).

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$(NH_4)_2SO_4$—3 % H_2SO_4 solution, which is connected to the cell by means of a 3 % $(NH_4)_2SO_4$—4% agar salt bridge. The indicator electrode system consists of two 6-in. lengths of 16-gauge platinum wire sealed into glass tubing in such a way that about 1/4 in. of each wire protrudes from its glass seal. These electrodes are mounted vertically through the rubber stopper so that all the exposed wire makes contact with the test solution. A 45-v battery, connected to the wires through a 20-megohm resistor, serves as the source of polarizing voltage. The solution is magnetically stirred.

The automatic coulometric titrator developed by Stelzner et al.[4] furnishes the constant current required and also automatically stops the flow of generating current when a preset end-point potential is reached. A clock is included in the circuit as a means of measuring the time during which current flows through the generating circuit.

C. Results

The precision of data taken by this method when solutions that contained various concentrations of chromium were analyzed is given in Table 2. This table shows that (1) as little as 4 μg of chromium(VI) can be titrated, but that much better precision is obtained when at least 10 μg of chromium(VI) are titrated by this method, (2) the ammonium persulfate treatment should be avoided when possible because it results in some loss in precision probably because of the increase in the number of operations, and (3) uranium and copper do not interfere under the conditions at which they were present.

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Table 2

Precision of Data Taken by the Coulometric Titration Method for Determination of Microgram Quantities of Chromium

Nine 1-ml aliquots were titrated in each case, except where indicated.

Approx. Conc. of Soln. Titrated, μg Cr/ml	S, %	Extreme Values from Average, %
100	0.35	± 0.5
50	0.5	± 1.0
10	0.8	± 1.0
10[a]	0.7	± 1.0
4[b]	2.0	± 2.5
4[c]	3.8	± 5.0

(a) Contained 40 mg of U and 2.5 mg of Cu per ml.

(b) Eleven 1-ml aliquots titrated.

(c) Obtained by treating 1 ml samples containing 2μg of chromium(III) per milliliter with $(NH_4)_2S_2O_8$.

Some typical results obtained by the titration of triplicate 1-ml aliquots of standard potassium dichromate solutions of various concentrations are listed in Table 3. The three analyses of each solution were made consecutively in the same "electrolyte" solution.

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Table 3

Typical Results of the Coulometric Titration of Standard Chromium Solutions

(One-milliliter aliquots were titrated in each case, triplicates being analyzed consecutively in one "electrolyte" solution. All standard solutions prepared from Bureau of Standards $K_2Cr_2O_7$.)

Cr Present, µg	Generation Time, sec	Generating Current, ma	Cr Found, µg	Avg., µg	Error, %
236.0	217.1	6.0	233.9		
	217.6	6.0	234.5	234.3	- 0.7
	217.7	6.0	234.6		
177.9	169.6	5.8	176.7		
	169.0	5.8	176.0	176.3	- 0.9
	169.1	5.8	176.2		
110.2	122.5	5.0	110.0		
	122.0	5.0	109.6	109.8	- 0.4
	122.4	5.0	109.9		
80.2	111.3	4.0	80.0		
	110.9	4.0	79.7	79.8	- 0.5
	111.0	4.0	79.7		
64.1	110.8	3.2	63.7		
	110.8	3.2	63.7	63.6	- 0.8
	110.3	3.2	63.4		

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Table 3, Continued

Cr Present, µg	Generation Time, sec	Generating Current, ma	Cr Found, µg	Avg., µg	Error, %
44.1	122.3	2.0	43.9	44.0	- 0.2
	122.8	2.0	44.1		
32.1	110.8	1.6	31.8		
	111.1	1.6	31.9	31.9	- 0.6
	111.1	1.6	31.9		
11.0	124.0	0.5	11.1		
	125.1	0.5	11.2	11.1	+ 0.9
	122.5	0.5	11.0		

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D. Procedure

Sections IV, V, VI, and VII of Method No. 9 0822012, "Chromium in Homogeneous Reactor Type Solutions, Coulometric Titration Method", as written for tentative issue to the ORNL Master Analytical Manual, are given in Apx. II.

Although the procedure was written specifically for use with the automatic coulometric titrator(4), the general titration procedure and principles will remain the same regardless of the instrumentation used.

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VI. Conclusions

The two methods discussed in this report were developed primarily for the use in analysis of HR type solutions. They have been recommended for this purpose, and are also recommended for the analysis of other solutions that contain small amounts of chloride or chromium. They are especially suited for the analysis of radioactive solutions.

These methods could probably be extended to the determination of even smaller quantities if a smaller cell could be designed that would adequately accommodate the various electrodes and salt bridges. The use of porous Vicor glass tubing instead of agar-type salt bridges to make electrical contact between separated electrodes could prove useful in this respect.

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APPENDIX I

Procedure for Coulometric Titration of Chloride

IV. APPARATUS

1. Automatic Coulometric Titrator and Accessory Apparatus. For description of this instrument see reference 3 (reference 4 of this report).

2. Potentiometer, Rubicon, providing measurement of voltages from 0 to 1.1 volt.

3. Accessory Apparatus, shown in Apx. I, and consisting of the following:

a. Generating Electrode System

(1) Silver Wire Anode, a 6-in. length of 14-gauge silver wire, coiled at one end to provide maximum contact with the test solution.

(2) Platinum Gauze Cathode, a fine platinum gauze cylinder, 1 cm high x 1 cm in diameter, is satisfactory; the dimensions are not critical.

(3) Salt Bridge, 3 % KNO_3 — 4 % Agar. Fit a 5-in. length of glass tubing into each end of an 8-in. length of 1/4-in. dia Tygon tubing. By applying suction to one end, fill this tubing with a nearly boiling solution of 3 g of reagent-grade KNO_3 and 4 g of agar-agar in 100 ml of water. Allow this hot solution to cool and to solidify in the tubing before it is used as the salt bridge.

b. Indicating Electrode System

(1) Silver Wire Indicator Electrode, a 6-in. length of 16-gauge silver wire which has been roughened with fine emery cloth.

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APPENDIX I.

IV. APPARATUS (Continued)

(2) Salt Bridge, similar to the one described in Section IV, 3, a (3) above.

(3) Saturated Calomel Reference Electrode. Thoroughly mix about 2 g of reagent-grade Hg_2Cl_2 with enough pure mercury to cover the bottom of a 125-ml Erlenmeyer flask. Place the mixture in the flask and add at least 50 ml of a saturated solution of reagent-grade KCl in distilled water. Add a slight excess of solid KCl and mix the contents of the flask. Allow the electrode to stand overnight before use.

c. Titration Vessel

(1) A 15-ml weighing bottle fitted with a rubber stopper for titration of less than 100 µg of chloride,

or (1a) A 50-ml beaker fitted with a rubber stopper for titration of more than 100 µg of chloride,

d. Ice-Water Jacket, a crystallizing dish of about 1-in. depth and 5-in. diameter.

e. Magnetic Stirrer, complete with glass-covered stirring bar.

V. REAGENTS

1. Ammonium Hydroxide Solution, approximately 7 % NH_3. Mix 25 ml of concentrated NH_4OH with 75 ml of distilled water.

2. "Electrolyte" Solution, 80 % CH_3OH — 5 % HNO_3. Prepare by mixing 20 ml of 1:4 HNO_3 with 80 ml of methanol.

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APPENDIX I

V. REAGENTS (Continued)

3. Hydroxylamine Hydrosulfate Solution, approximately 10 % $NH_2OH \cdot H_2SO_4$. Dissolve 10 g of $NH_2OH \cdot H_2SO_4$ in enough distilled water to make 100 ml of solution.

VI. SAMPLING

This procedure was developed on the basis of using 1-ml portions of the sample solution for titration. This is a convenient volume because it allows for duplicate and triplicate analyses of a sample in one "electrolyte" solution. Larger or smaller volumes can be used as long as the total amount of chloride titrated is at least 4 µg. Test portions larger than 4 ml are not recommended because the total solution volume in the cell would then be too large for thorough mixing to be maintained during the titration.

VII. PROCEDURE

1. Move the "Power" switch of the titrator to the "On" position and allow five minutes for the instrument to warm up.

2. Place 3 ml (NOTE a) of the "electrolyte" solution in the cell. Add about the same quantity of chloride as is expected to be present in the sample; add it as a dilute HCl solution. If chromium is present in the sample to be titrated, add 2 drops of 10 % $NH_2OH \cdot H_2SO_4$ solution.

3. Position the cell so that good contact is made between the solution and both the generating and the indicating electrode systems.

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APPENDIX I

VII. PROCEDURE (Continued)

4. Place the ice-water jacket around the cell and adjust the speed of the magnetic stirrer for adequate mixing.

5. Allow the solution to cool three minutes; meanwhile,

6. Adjust the automatic cutoff control so that cutoff occurs at +0.230 volt when the indicated potential is changing in the 0- to +1.4-volt direction, and

7. Adjust the current as indicated on the ammeter to a value such that at least 150 seconds will be required to titrate the sample, and finally,

8. Move the "Selector" control to the "Automatic Cutoff with Delay" position.

9. Move the "Titrate-Standby" control to the "Titrate" position and allow the titration to proceed automatically until the time interval during which no current flows increases to 1 1/2 minutes. This is considered to be the end point.

10. Move the "Titrate-Standby" control to the "Standby" position .

11. Pipet the test portion of the sample (see Section VI) to the above solution and cool the solution for an additional two minutes (NOTE c).

12. Zero the clock.

13. Move the "Titrate-Standby" control to the "Titrate" position and allow the titration to proceed automatically to the end point as in Step 9 above. Do not disturb the current-adjustment controls during this titration.

14. Return the "Titrate-Standby" control to the "Standby" position.

15. Record the exact current used in milliamperes and the time in seconds required to titrate the sample (NOTE d).

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APPENDIX I

VII. PROCEDURE (Continued)

16. When the cell is not in use, leave it in position and containing 5 ml of 1:100 HNO_3.

Calculations

$$\text{Electrolyzed equivalents} = \frac{I(\text{amp}) \times t\ (\text{sec})}{96{,}500}$$

$$\frac{\text{Cl, } \mu g}{10^6\ \mu g/g} \times \frac{1}{35.46\ g/eq.} = \frac{I\ (ma) \times t\ (sec)}{1000\ ma/amp \times 96{,}500}$$

$$\text{Chloride Titrated, } \mu g = 0.3675 \times I\ (ma) \times t\ (sec).$$

$$\text{Chloride in Sample, } \mu g/ml = \frac{0.3675 \times I\ (ma) \times t\ (sec)}{\text{volume sample taken, ml}}.$$

Notes

(a) If a 50-ml beaker is used as the titration cell, add sufficient "electrolyte" solution to make contact with both the generating and the indicating electrode systems.

(b) During this titration, readjust the current to the exact value desired. Make this adjustment while measuring the current by means of a potentiometer which measures the IR drop across the standard 100-ohm resistor that is incorporated into the generating circuit. The milliamperes of current flowing will equal ten times the IR drop measured in volts.

(c) If chromium is present in the sample, readjust the automatic cutoff control so that cutoff occurs at +0.230 volts vs S.C.E. plus the appropriate

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APPENDIX I

VII. PROCEDURE

Notes (Continued)

end-point potential correction. See Table I, Section III, Status, for these corrections.

(d) If chromium is not present in the sample and duplicate or triplicate analyses are desired, the next aliquot of the sample may be added to the solution just titrated and analyzed by following Steps 10 through 14.

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APPENDIX II

Procedure for Coulometric Titration of Chromium

IV. APPARATUS

1. Automatic Coulometric Titrator and accessory apparatus. For description of this instrument, see reference 4.

2. Potentiometer, Rubicon, providing for measurement of voltages from 0 to 1.1 v.

3. Accessory apparatus, shown in Apx. II, and consisting of the following:

a. Generating Electrode System

(1) Platinum "Flag" Generating Electrode, a 1 x 2 cm strip of platinum foil joined to a 6-in. length of 16-gauge platinum wire.

(2) Platinum Gauze Electrode, a fine platinum gauze cylinder, 1 cm height x 1 cm in diameter, is satisfactory; the dimensions are not critical.

(3) Salt Bridge, 3 % $(NH_4)_2SO_4$— 4 % Agar. Fit a 5-in. length of glass tubing into each end of an 8-in. length of 1/4-in. dia Tygon tubing. By applying suction to one end, fill this tubing with a nearly boiling solution of 3 g of reagent-grade $(NH_4)_2SO_4$ and 4 g of agar-agar in 100 ml of distilled water. Allow this hot solution to cool and to solidify in the tubing before it is used on the salt bridge.

b. Indicating Electrode System

(1) Platinum Wire Electrodes. Seal each of two 6-in. lengths of 16-gauge platinum wire into a 5-in. length of glass tubing in such a way that about 1/4 in. of wire protrudes from the glass seal.

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APPENDIX II

IV. APPARATUS (Continued)

(2) Battery, 45-volt, Burgess 230NX "B" battery.

(3) Resistor, 20-megohm, 1/4 watt.

(4) Two-way Switch with four lead wires.

c. Titration Cell, a 15-ml weighing bottle fitted with a rubber stopper.

d. Magnetic Stirrer, with glass-covered stirring bar.

V. REAGENTS

1. Ammonium Persulfate Solution, 20 % W/V $(NH_4)_2S_2O_8$. Prepare daily as required from reagent-grade $(NH_4)_2S_2O_8$.

2. "Electrolyte" Solution, approximately 22 % $FeNH_4(SO_4)_2 \cdot 12\ H_2O$. Prepare by mixing 90 ml of the $FeNH_4(SO_4)_2$ solution (reagent 3) with 10 ml of concentrated HCl.

3. Ferric Ammonium Sulfate Solution, approximately 24 % $FeNH_4(SO_4)_2 \cdot 12\ H_2O$. Prepare by dissolving 12 g of reagent-grade $FeNH_4(SO_4)_2 \cdot 12\ H_2O$ in 200 ml of water that contains 14 ml of 50 % H_2SO_4 and diluting the solution to 500 ml.

VI. SAMPLING

The procedure is best suited to the titration of 1-ml portions of solutions that contain not less than 4 µg of Cr(VI) per ml. Duplicate or triplicate analyses of the same solution can then be run in the same "electrolyte" solution.

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APPENDIX II

VI. SAMPLING (Continued)

Larger or smaller volumes may, however, be taken in order to titrate a total of at least 4 µg of Cr(VI). The use of portions larger than 4 ml is not recommended since the total volume would be too large for thorough mixing to be maintained during the titration. Best results are obtained when a total of at least 10 µg of Cr(VI) is titrated.

VII. PROCEDURE

A. Preliminary Oxidation of Sample

If any chromium is present as chromic ions, preliminary oxidation to chromium(VI) is necessary before the titration is run. This can be done conveniently as follows:

1. From the sample solution, pipet a 1-ml portion which contains 10 to 100 µg of Cr into a 5-ml volumetric flask.

2. For every 20 µg of Cr expected in the sample, add approximately 200 µl of 20 % $(NH_4)_2S_2O_8$ solution.

3. Add approximately 50 µl of saturated Ag_2SO_4 solution.

4. Place the flask on a hot plate, bring the solution to a boil, and boil it gently for 5 to 7 minutes.

5. Remove the flask from the hot plate, cool the solution to room temperature, and dilute the solution to 5 ml with distilled water.

6. Mix the solution thoroughly.

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APPENDIX II

VII. PROCEDURE (Continued)

B. Analysis of Sample

1. Turn the power switch of the titrator on and allow 5 minutes for the instrument to warm up.

2. Pipet 3 ml of "electrolyte" solution into the titration cell.

3. Add a 1-ml volume of a dichromate solution which contains about the same amount of Cr(VI) as that expected in the sample portion to be titrated.

4. Place the stirring bar in the cell.

5. Position the cell so that good contact is made between the solution and both the generating and indicating electrode systems.

6. Adjust the speed of the stirring motor to give adequate mixing of the solution (NOTE a).

7. Move the electrode polarizing switch to the "polarize" position.

8. Adjust the automatic cutoff control so that cutoff occurs at +0.280 volt when the indicated potential is changing in the +1.4- to 0-volt direction.

9. Adjust the generating current to a value such that not less than 100 seconds will be required to make the titration (NOTE b).

10. Move the selector switch to the "Automatic Cutoff-No Delay" position.

11. When the indicated potential of the solution reaches +0.360 volt or more, move the titrate switch to the "Titrate" position and allow the titration to proceed automatically to cutoff (NOTE c).

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APPENDIX II

VII. PROCEDURE

B. Analysis of Sample (Continued)

12. Move the titrate switch to the "Stand-by" position and the electrode polarizing switch to the "Shorted" position.

13. Add a portion of the sample that is estimated to contain not less than 4 µg of Cr(VI) (NOTE d). See Section VI, Sampling.

14. Zero the clock.

15. Move the electrode polarizing switch to the "Polarize" position.

16. When an indicated potential of +0.360 volt or more is reached, move the titrate switch to the "Titrate" position and allow the titration to proceed automatically to cutoff. Do not disturb the generating-current controls.

17. Record in milliamperes the exact generation current used and the time required for titration of the sample to cutoff.

18. Move the titrate switch to the "Stand-by" position and the electrode polarizing switch to the shorted position (NOTE e).

19. Fill the cell with distilled water and leave it in position when it is not in use.

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APPENDIX II

VII. PROCEDURE (Continued)

Calculations

(1) Electrolyzed equivalents = $\frac{I\ (amp) \times t\ (sec)}{96{,}500}$

$$\frac{Cr,\ \mu g}{10^6\ \mu g/g} \times \frac{1}{17.67\ g/eq.} = \frac{I\ (ma)}{1000\ ma/amp} \times \frac{t\ (sec)}{96{,}500}$$

Chromium(VI) Titrated, $\mu g = 0.1796 \times I\ (ma) \times t\ (sec)$.

(2) A = ml of sample treated with $(NH_4)_2S_2O_8$ and diluted to 5 ml,

B = ml taken for titration

$$\text{Chromium in Sample, } \mu g/ml = \frac{0.1796 \times I\ (ma) \times t\ (sec)}{B} \times \frac{5}{A}.$$

Notes

(a) The same stirring speed should be used for all titrations.

(b) This may be estimated by use of the equation used to calculate the final result.

(c) During this titration, readjust the generating current to the exact value desired. This adjustment should be made while measuring with a potentiometer the IR drop across the standard 100-Ω resistor that is incorporated in the generating circuit. The milliamperes of current flowing will be ten times the voltage reading on the potentiometer.

(d) Although as little as 4 μg of Cr(VI) can be titrated, much better results can be obtained with 10 μg or more of Cr(VI).

(e) If the sample is to be run in duplicate or triplicate, the next portion of the sample may now be added and titrated according to Steps 13 through 18.

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