Retrospective Theses and Dissertations

Iowa State University Capstones, Theses and Dissertations

1968

High precision constant current coulometric assay of primary standard oxidizing agents

John William Knoeck
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Analytical Chemistry Commons

www.manaraa.com

HIGH PRECISION CONSTANT CURRENT COULOMETRIC

ASSAY OF PRIMARY STANDARD OXIDIZING AGENTS

by

John William Knoeck

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1968

TABLE OF CONTENTS

INTRODUCTION

During the past fifteen years a curious and instructive controversy has swirled about the oxidation-reduction primary standard ammonium hexanitratocerate and in particular about the thorium present in various preparations of the compound. Ammonium hexanitratocerate was first proposed as a primary standard by Smith, Sullivan and Frank (25). In a second paper, Smith and Fly (24) using weight buret titrations of NBS 40e Sodium Oxalate and NBS 83a Arsenic Trioxide found for two commercial lots of ammonium hexanitratocerate a purity of 99.98 per cent, the average standard deviation over five sets of analyses (two products, two primary standards, one product after storage for one year) being 0.010 per cent, that is, an average standard deviation of 10 parts per 100,000. Commercial preparations of ammonium hexanitratocerate, however, were later shown to contain variable and often appreciable amounts of thorium: by Voigt[1] by measurement of the radioactivity, by Fassel (6) by emission spectrographic analysis, by Salutsky, Kirby and Quill (20) by separation and identification of the radium 224 daughter product of thorium. The problem is one of reconciling the high purity reported with a significant thorium

---

[1] Voigt, A., Ames, Iowa, Institute for Atomic Research. Data from unpublished research. Private communication. 1967.

content, as high in some lots as several tenths of one per cent.

Smith's original work (25) was done with small amounts of materials of which none remains. No lot numbers were recorded for the commercial preparations analyzed by Smith and Fly (24) and again no material was preserved. Direct examination of the original materials is thus precluded but two recent papers throw light on the problem. Smith (23) subjected a batch of ammonium hexanitratocerate to a series of recrystallizations from concentrated nitric acid. The thorium in successive crops was determined by emission spectrographic analysis and neutron activation analysis. The thorium content dropped very slowly; starting with a material bearing 0.4 per cent of thorium, the thorium in the materials obtained from four successive re-crystallizations was 0.12, 0.041, 0.011 and 0.005 per cent Th. In the other paper Fassel, Jasinski, DeKalb and Lucas (6) show that the failure to find thorium in earlier preparations may have resulted from misidentification of the lines of the spectra of cerium and of thorium. It is of course possible that the commercial preparations examined by Smith and Fly (24) were free of thorium, either because the starting materials were fortuitously free of thorium or because these particular lots were the result of a sufficient number of recrystallizations not given other commercial lots.

The controversy surrounding the use of ammonium

hexanitratocerate makes it desirable to examine the reliability of this compound as a primary standard and the relationship between the oxidizing capacity and the thorium content.

Potassium dichromate has been used extensively as a primary standard oxidizing agent. It is readily available in certified high purity from the National Bureau of Standards. The reaction of it as an oxidizing agent is well characterized, and its reputation as a primary standard is unquestioned. Potassium dichromate was therefore chosen as the ideal primary standard oxidizing agent to which ammonium hexanitratocerate could be compared.

The use of potassium dichromate as a primary standard acid, while not so widely recognized, was proposed by Richter (18) as early as 1882. Kolthoff and Vogelenzang (10) investigated the titrations of dichromate with alkali and report that the neutralization reaction was slow. When the proper indicator, thymolphthalein, was used however, these workers reported "serviceable" results. In the present work the utility of potassium dichromate as a primary standard acid was re-examined. Preliminary work with the usual glassware of volumetric analysis showed that, within experimental error (1 part in 1,000), identical results were obtained for the standardization of a 0.1 N sodium hydroxide solution using potassium acid phthalate and potassium dichromate. The slow neutralization reported by Kolthoff was not observed, although the first green color

at the end-point (basic blue color of thymolphthalein super-
imposed on a yellow color of chromate) was sharp and distinct
but not striking. The feasibility of high precision neutrali-
zation titrations of dichromate was thus apparent.

In this work the purity of NBS 136b potassium dichromate
has been determined by coulometric titration with both electro-
generated iron(II) and with electrogenerated hydroxide ion.
The purities as determined by each of these methods were in
agreement with and confirmed the results of Marinenko and
Taylor (15). The difference between the coulometric assay,
99.975 per cent, and 100.000 per cent is a matter of concern
and supplementary work was carried out to show that the differ-
ence, 0.025 per cent, consists of metallic impurities (about
0.0055 per cent) and water (0.0200 per cent). The metallic
impurities were detected and determined by mass spectro-
graphic analysis by others in this laboratory. The water was
determined by weight loss on prolonged drying at 250°C.

The purities of several preparations of ammonium hexanitra-
tocerate have been determined by constant current coulometric
titration with electrogenerated iron(II). The results make it
very certain that the purity, as determined by the oxidizing
capacity, falls off with increasing thorium content. Given a
thorium-free preparation, however, the coulometric assay indi-
cates a definite composition and a purity which places ammonium
hexanitratocerate on a par with potassium dichromate as a
primary standard.

Constant current coulometry represents one of the most precise techniques at the disposal of the analyst for determining the purity of materials and was therefore chosen as the analytical technique to be used in this work. Coulometric titrations require only the measurement of the physical quantities of mass, time, resistance and potential all of which can be measured with great accuracy and relative ease. Coulometric titrations with precisions of a few parts in 100,000 have been obtained by several workers: by Taylor and Smith (28) in the analysis of benzoic acid, potassium acid phthalate, adipic acid, constant boiling hydrochloric acid, and sodium carbonate; by Marinenko and Taylor (14) of sodium chloride, sodium bromide and potassium iodide; by Marinenko and Taylor (15) of potassium dichromate; by Cooper and Quayle (3) of sodium carbonate; by Eckfeldt and Shaffer (5) of potassium acid phthalate and constant boiling hydrochloric acid; by Marinenko and Taylor (16) of arsenic trioxide and elemental iodine. The method has been so successful that the coulomb has been proposed as the ultimate primary standard (27, 3).

In the work being described here, apparatus for high precision, constant current coulometry has been assembled from commercially available components (Leeds and Northrup Company, Philadelphia, Pennsylvania, reference (5)). This apparatus has been used to determine the purities of ammonium hexanitratocerate and potassium dichromate.

As will be shown in a subsequent discussion of the experimental work, the measurements of each of the terms in Faraday's law of electrolysis, current, mass, time, the value of the Faraday, and the equivalent weight, could be made with errors of less than two parts in 100,000. This uncertainty represents the limits to which the precision and accuracy of constant current coulometry can be pushed at the present time. Precisions and accuracies of the order of a few parts in 100,000 were chosen as the goal for the present work.

Coulometric titrations are of two types: internal and external generation of titrant. In the former technique the titrant is generated and the titration reaction carried out in the same cell. This technique was used to carry out reductimetric titrations of potassium dichromate and ammonium hexanitratocerate with electrogenerated iron(II). The problems encountered in coulometric titrations with internal generation of titrant are: 1) insuring the separation of anode and cathode reaction products while maintaining electrical contact; 2) choosing conditions such that the current efficiency is one hundred per cent, and 3) of finding a suitable method of end-point detection. Each of these factors is discussed in the appropriate following section with particular emphasis being given the problem of end-point detection in view of the participation of platinum indicator electrodes in oxidation-reduction reactions.

The high precision constant current coulometric titration of potassium dichromate, or more correctly its hydrolysis product, with electrogenerated hydroxide ion posed a special problem. Hydroxide ion is produced by the electrochemical reduction of water, and since dichromate would be reduced in preference to water, external generation of titrant is necessary. Ordinarily external generation is carried out at electrodes sealed into tubes through which an electrolyte solution flows, the generated titrant being allowed to drip from the tube into the titration cell. However, in view of the extended period of time required for a high precision titration, eight hours or so, the continual flow of solution into the cell made external generation impractical. A new cell was designed to circumvent this difficulty. The bulk of the hydroxide ion was generated in one of two connecting chambers; the sample is placed in the other. When nearly all of the titrant has been generated, the solutions were mixed; the titration was then completed with an external dripping electrode. With this new cell, it was possible to titrate potassium dichromate as an acid with high precision. The problems of 1) separating anode and cathode and 2) detecting the end-point are present in work with the new cell, however, in the special case of the generation of hydroxide ion, current efficiency is necessarily one-hundred per cent in the absence of impurities.

The assay of the materials reported in this work suggest that purities a few hundredths of a per cent below the theoretical might be expected for primary standards. In the case of potassium dichromate low assay has been shown to be largely due to occluded water although the presence of other impurities was detected. In general the analysis of primary standard materials reported by other workers are also a few hundredths of a per cent below the theoretical. Unless the analyst performs painstaking purifications or obtains certified materials, there is always some question as to the reliability of a primary standard material. In the former case, the analyst frequently lacks the time or the facilities to perform the purification. In the latter, the desired material is frequently unavailable in certified purity and is always expensive when available. By using constant current coulometry, the analyst can perform nearly all the types of titrations normally carried out volumetrically. In view of the success of the constant current coulometric method of analysis, it is now possible to adopt the coulomb as the ultimate primary standard for chemical analysis.

EXPERIMENTAL WORK

Apparatus and Materials

Measurement of current

A Leeds and Northrup Company "Coulometric Analyzer" (L
and N catalog number 7960) was used as the source of constant
current. The L and N 7960 has three output currents of approxi-
mately 64.3, 6.43 and 0.643 mamps., respectively. Current was
determined by measuring the voltage drop across a resistance of
19.99979 ohms, this resistance having been specially constructed
and calibrated by the Leeds and Northrup Company (L and N Cat.
No. 4025-B-S). Potential was measured with a Leeds and North-
rup "Potentiometer Facility" (Cat. No. 7555) consisting of a
Type K-5 potentiometer, a null detector (Cat. No. 9834-1 D. C.),
constant voltage supply (Cat. No. 9878), and a Weston standard
cell. Voltage regulators were used to eliminate fluctuations
in the line voltage. Deviations of $\pm$ 0.002 per cent in the IR
drop at maximum current flow could be detected with this
arrangement. The manufacturer states (5) that the 7960 current
source produces an appreciable A. C. ripple but that it falls
within the integrating capabilities of the null detector.

The 4025-B-S resistor was immersed in a constant tempera-
ture bath of mineral oil but even with the bath providing a
heat sink, the temperature of the resistor rose with the
passage of current. A temperature increase of about 1° occurred
in the first few minutes of current passage with the output of

the constant current source at its maximum, 64.3 mamps. After the first few minutes, the temperature increase slowed somewhat and after about 15 minutes, the temperature reached a steady state 1.5° above the temperature of the bath. Most of the temperature increase took place during pretitration as described below, so that the change in resistor temperature during an actual titration never amounted to more than a few tenths of one degree. Nevertheless, each time the IR drop was measured, the temperature of the resistor was noted and the actual resistance calculated using temperature coefficients provided by the manufacturer:

$$R_t = 19.9997 \left[1 + 0.000002 \, (t-25) - 0.0000005 \, (t-25)^2\right]$$

Two Weston cells were used alternately. Each cell was calibrated every three months against a third resident cell in the Iowa State University Instrument Shop. This third cell was periodically calibrated against a fourth cell which was sent to the National Bureau of Standards for calibration at intervals of six months.

The Type K-5 potentiometer was calibrated at the standardizing laboratory of the Leeds and Northrup Company. At the potentials measured, no corrections were required.

Measurement of time

The L and N coulometric analyzer is equipped with a synchronous timing motor and a counter reading directly in microequivalents. To eliminate the consequences of possible

variations in the frequency of the alternating current main the counter may be driven alternatively by a frequency standard. A frequency standard manufactured by American Time Products, Woodside, New York, Model 2005A, was used in this work. The frequency standard driven counter was calibrated using the time signals of Radio Station WWV of the National Bureau of Standards. Six calibration runs were made over elapsed times ranging from 24 to 72 hours. The number of counts per minute for these six runs agreed to within one part in one million. The time calibration was checked periodically during the course of the work.

Measurement of mass

The standards of mass used were one-gram and ten-gram Class M weights calibrated by the National Bureau of Standards. Weighings were made on an Ainsworth TCX equal-arm balance to the nearest 0.01 mg. All weighings were made by substitution, that is, the empty sample boat and the calibrated weight of the appropriate size were weighed together, the calibrated weight was removed, and sample was added to the boat until the weight was equal to the weight removed to within one milligram. Weighings were corrected to weight in vacuum using as the density of potassium dichromate 2.69 and of ammonium hexanitratocerate 2.61.

The weights of the materials analyzed were chosen to require a sufficient number of coulombs for titration to permit measurement to at least one part in 100,000; one-gram samples

of potassium dichromate (equivalent weight 49.0320) and ten-
gram samples of ammonium hexanitratocerate (equivalent weight
548.23) were used.

Calculation of equivalents

For the conversion of coulombs to electrochemical equiva-
lents, the current value of the Faraday was used, 96,487.0
± 1.2 coulombs per equivalent, as measured by Craig, Hoffman,
Law, and Hamer (4) and corrected to the C^{12} atomic weight
scale (14). The equivalent weights used, 49.0320 for potassium
dichromate and 548.23 for ammonium hexanitratocerate, were
calculated using the values of the 1961 Report of the Inter-
national Commission on Atomic Weights (7).

Titration cell, electrodes, electrolytes for reductimetric
titrations

Reductimetric titrations were carried out in a cell simi-
lar to that of Eckfeldt and Shaffer (5). The cell consisted of
a 1-liter, tall form beaker fitted snugly with a cover of poly-
ethylene through which passed the generating reference and
indicator electrodes, shield tube, and nitrogen inlet tube.
Cathode and anode were separated by two concentric shield
tubes, the bottom of each being provided with ultrafine, glass
frits as shown in Figure 1. The shield tubes are the essential
feature of the Eckfeldt and Shaffer cell and as in their work,
a head was maintained on the electrolyte in the intermediate,
bridge solution such that flow of this electrolyte was into
anolyte and catholyte, thus insuring that no transfer of

Figure 1.   Coulometric titration cell.   A. Platinum cathode;
            B. Platinum anode; C, D. Ultrafine, glass frits on
            bottom of shield tubes; E. Nitrogen inlet; F, G.
            Indicator electrodes, either two platinum foils or
            a platinum foil and a s.c.e.; H. Magnetic stirring
            bar; I. Polyethylene cover; J. 1-Liter, tall-form
            beaker.

14

A

B

C

D

E

F

G

H

J
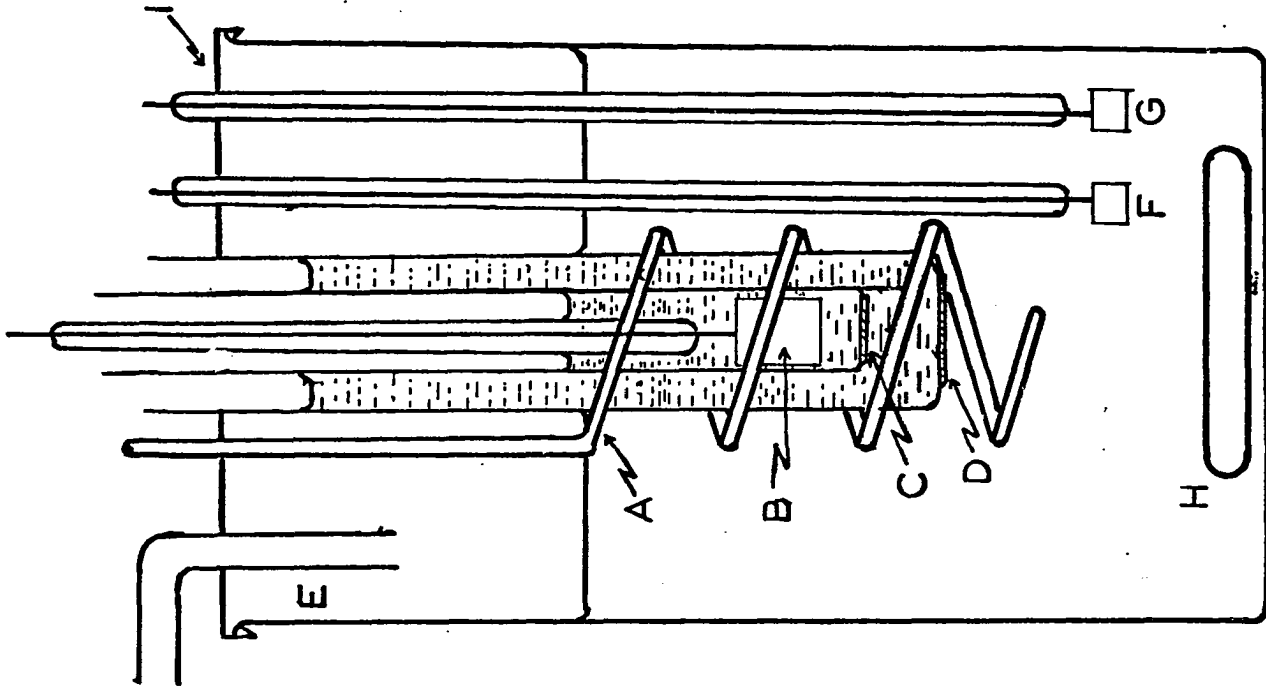
material out of either cathode or anode chamber occurred.

The working cathode was a helix of platinum wire with a surface area of 26 cm². The anode was a platinum foil with a surface area of 2.5 cm².
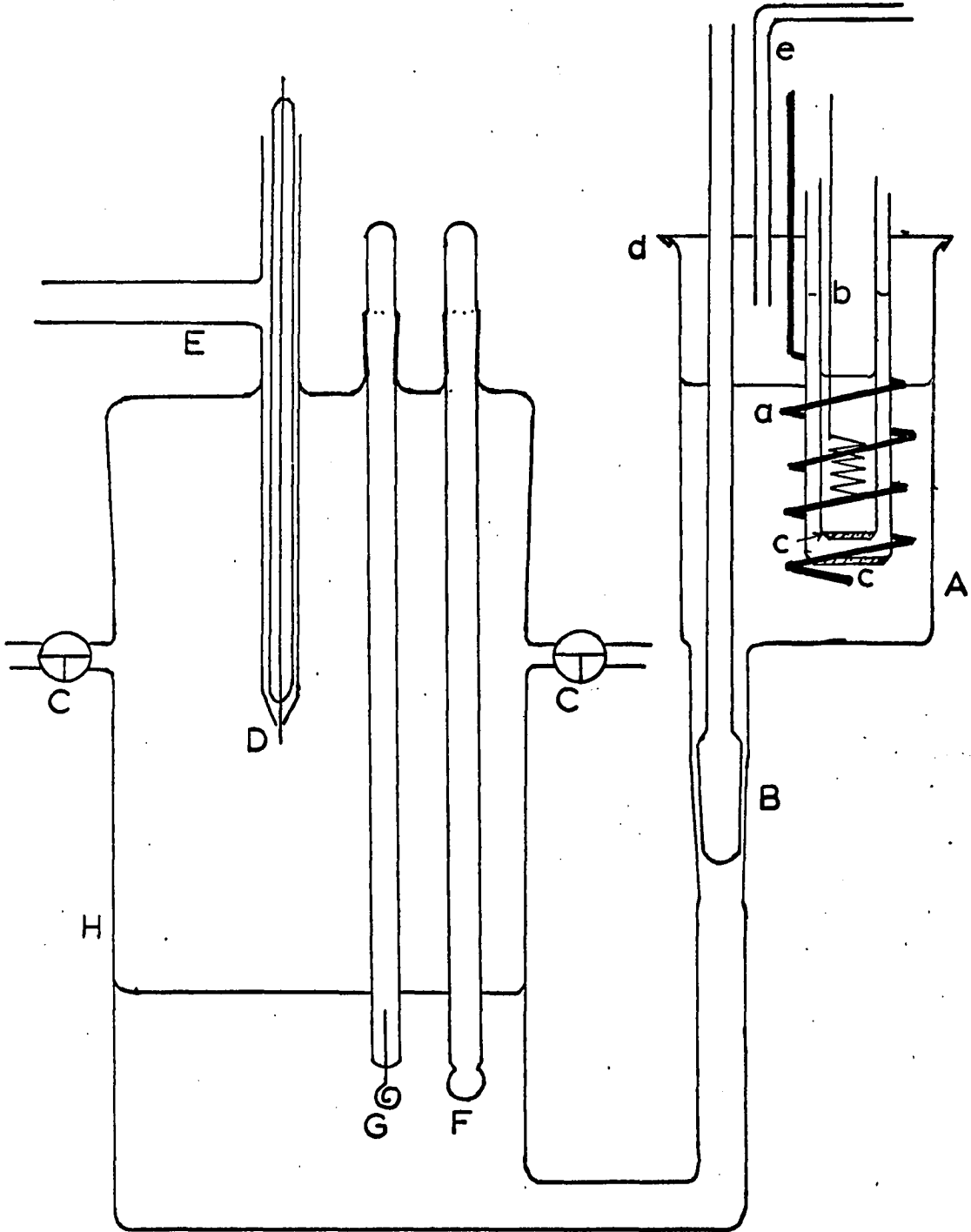
The catholyte consisted of 500 ml. of a solution of 0.20 M in iron(III) perchlorate and 4.0 M in perchloric acid. The analyte, and also the electrolyte in the intermediate chamber, was a solution 1.0 M in sodium perchlorate and 0.1 M in perchloric acid.

Titration cells, electrodes, electrolytes for neutralization titrations

The cell used for the titrations of potassium dichromate as an acid is shown in Figure 2. This cell consisted of two chambers, A and H, separated by a polished ground glass joint B. Chamber A was similar in construction to the cell shown in Figure 1, the total volume of A being 300 ml. The bulk (99.95%) of the required hydroxide ion was generated in chamber A. The sample was dissolved in chamber H. Upon opening valve B the solutions mixed and by using nitrogen pressure and stopcocks C, the solution could be alternately forced into chamber A and allowed to flow back into chamber H thus insuring that the solutions were well mixed.

The titration was completed by generating the final hydroxide ion at a small platinum wire cathode D. Solution flowed over the cathode from a reservoir through glass tubing E. The anode was located in a side arm connected to tube E

Figure 2. Coulometric titration cell for external genera-
tion of titrant. A: Generation chamber; a. Plati-
num cathode; b. Platinum or silver anode; c. Ultra-
fine glass frits on bottom of shield tubes; d. Poly-
ethylene cover; e. Nitrogen inlet; B. Polished,
ground-glass standard taper valve; C. 3-Way stop-
cocks; D. Platinum wire cathode for completion of
titration; E. Glass tubing to solution reservoir
(counter electrode to D located in side-arm on tube
E); F and G. Glass-reference indicator electrodes;
H. Reaction chamber.

through an ultra-fine glass frit.

The catholyte consisted of 120 ml. of a 1.0 M solution of sodium perchlorate. The anolyte consisted of either a 1.0 M solution of potassium chloride, in which case a silver wire anode was used, or a 1.0 M solution of sodium perchlorate, in which case a platinum wire anode was used. The bridge tube in chamber A contained a solution identical to the catholyte.

Samples and Reagents

Potassium dichromate NBS 136b

Potassium dichromate was dried at 110°C for 24 hours and stored in vacuum over anhydrous magnesium perchlorate.

Ammonium hexanitratocerate

Six lots of ammonium hexanitratocerate were obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio, the material having been manufactured at various times from 1952 to 1967; a seventh specimen (C of Table 4) was prepared from basnaesite. Each specimen was dried at 70°C for 24 hours and stored in vacuum over anhydrous magnesium perchlorate.

Specimen C was prepared from a rare earth oxide concentrate obtained from the thorium-free mineral basnaesite, $CeFCO_3$. The rare earth oxide was partially dissolved in 2 liters of boiling nitric acid. The solution obtained was filtered and concentrated to 1 liter by boiling. The cerium(IV) in a small aliquot of the solution was determined by titration

with ferrous sulfate. The theoretical amount of ammonium nitrate was then added and ammonium hexanitratocerate caused to crystallize by cooling. The product was collected on a fritted glass funnel and washed with concentrated nitric acid. The ammonium hexanitratocerate obtained in this way was re-crystallized five times from concentrated nitric acid and dried at 55° under vacuum for 48 hours.

Ferric perchlorate

Commercial samples were found to contain appreciable amounts of chloride and the ferric perchlorate used in the catholyte was prepared by dissolving individual 2-gram portions of electrolytic iron (G. Frederick Smith Chemical Company) in 50 ml. of 72 per cent perchloric acid and heating to boiling. By cooling the solutions quickly the resulting precipitate of ferric perchlorate was chloride free.

Nitrogen

Commercial "Prepurified" cylinder nitrogen was passed successively through scrubbers containing 1) distilled water; 2) vanadium(II) sulfate in 1 M sulfuric acid over amalgamated zinc (17); 3) alkaline permanganate (to insure the absence of hydrogen sulfide sometimes generated in the preceding oxygen absorption scrubber), and 4) a solution 0.20 M in iron(III) perchlorate and 4.0 M in perchloric acid or 1.0 M $NaClO_4$ (identical with catholyte). In reductimetric titrations, the nitrogen was initially passed through a tube containing

ascarite to remove carbon dioxide.

Water

    All solutions were prepared using distilled, deionized water further redistilled over alkaline permanganate.

Procedure

Reductimetric titrations with electrogenerated iron(II)

    A sample was weighed to the nearest 0.01 mg. into a platinum or glass boat using the substitution method. The boat was suspended by a platinum wire above the catholyte and held there while the pretitration was carried out and the major part of the iron(II) needed for the titration was generated. These three operations were carried out as follows. Nitrogen gas was bubbled through the catholyte for at least one hour; the nitrogen inlet tube was then raised above the catholyte and the flow of nitrogen reduced so that a small stream of nitrogen impinged gently on the surface of the catholyte. A small amount of the oxidizing agent (about 2 mg. of potassium dichromate or 18 mg. of ceric ammonium sulfate (about 40 microequivalents)) was added to the catholyte. The solution was stirred for about 5 minutes and the oxidizing agent titrated to well past the equivalence-point using the high current output of the constant current source. The procedure was repeated three times to insure that any oxidizable or reducible impurities in the catholyte were removed. A fourth addition of oxidizing agent was then made to the catholyte and the

titration carried out using the 0.643 mamp. output of the constant current source. The last pretitration was carried out by passing the current for short intervals, and after each, measuring the amperometric current passing the end-point detection electrodes (see following section on end-point detection). The titration was carried beyond the end-point and the final reading on the counter was recorded. The counter was then reset to zero and iron(II) generated using 64.3 mamp. This was continued until about 99.8 per cent of the iron(II) needed for the weight of sample taken was generated. The reading of the counter was again recorded and the counter re-set at zero. The boat and sample were lowered into the catholyte and after the sample had dissolved, the titration was continued using the 0.643 mamp. current and the same procedure for locating the end-point. Counter readings were then converted to seconds.

Weights of both the potassium dichromate and the ammonium hexanitratocerate were chosen so that about 20,000 microequivalents were titrated, about eight hours being required for the titration at the 64.3 mamp. current. During the titration the IR drop across the standard resistor was measured every 15 minutes or so. The temperature of the resistor was noted each time the IR drop was measured. The nominal value of the resistance was corrected to the temperature at which the IR drop was measured as described above, and the current calculated. The thirty or so measurements of the current

obtained during a given titration seldom varied more than 8 parts in 100,000, and the relative standard deviation of a set of values never exceeded 1 part in 100,000. Using the average value of the current and the number of seconds indicated by the standard frequency driven counter the number of coulombs passed at 64.3 mamp. was calculated. In a similar manner the coulombs passed at the lower current was determined by summing the counter readings for the current passed after the end-point in the pretitration and in approaching the end-point in the actual titration. The IR drop at the lower current was usually measured 7 to 10 times during each approach to an end-point. The precision of the measurement of the lower current was, of course, somewhat poorer, on the order of 10 parts in 100,000. However, only one or two one-thousandths of the total coulombs were passed at low current and the uncertainty introduced was negligible.

Neutralization titrations with externally electrogenerated hydroxide ion

About two liters of a 1.0 M sodium perchlorate solution was oxidized electrolytically to pH 5.5 at a platinum anode immersed in a covered four liter beaker. Nitrogen gas was passed over the stirred solution for at least one hour to remove dissolved carbon dioxide. The polarity of the electrodes was reversed and the solution reduced electrolytically to pH 7.00 ± 0.05 and transferred to a reservoir connected

to the small external generating electrode, D in Figure 2.
The solution in the reservoir was kept under nitrogen pressure
to prevent the absorption of carbon dioxide from the atmos-
phere.

A volume of 150 ml. of a 1.0 M sodium perchlorate solu-
tion was introduced into the external generation chamber A in
Figure 2, and titrated coulometrically to pH 5.5. Nitrogen,
free from oxygen and carbon dioxide, was passed over the solu-
tion for at least one hour to remove dissolved carbon dioxide.
The polarity of the generating electrode was reversed and the
acid solution titrated coulometrically to pH 8.5. The above
procedure, that is alternate oxidation and reduction, was re-
peated three times to insure the removal of electroactive im-
purities. The final step was always the titration of an acid
solution to pH 7.00 $\pm$ 0.01. Valve B in Figure 2 was then
opened and the solution allowed to flow into the titration
chamber H. A few crystals of potassium dichromate were added
to the solution in the titration chamber and the resulting
solution titrated with electrogenerated hydroxide ion using
the small generating electrode, D in Figure 2, and the 0.643
mamp. output of the constant current source. The pretitration
was carried out by passing current for short intervals and,
after each, measuring the pH of the solution (see following
section on end-point detection). The titration was carried
slightly beyond the end-point and, as in the reductimetric
titrations, the amount of excess hydroxide ion was added to the

amount generated during the titration itself. The solution
in the titration chamber was now ready for the introduction
of the sample.

A volume of 150 ml. of sodium perchlorate was placed in the
generating chamber of the cell, A in Figure 2. Carbon dioxide
was removed and the solution titrated to pH 7.00 ± 0.01 by the
procedure just described. The counter of the constant current
source was set to zero and 99.9 per cent of the theoretical
hydroxide ion was generated using the 64.3 mamp. output of the
constant current source. The counter reading was recorded and
the zero reset. The sample, weighed by difference into a glass
boat, was lowered into the titration chamber, H in Figure 2.
After the sample had dissolved, valve B was opened and the
hydroxide solution allowed to flow into chamber H. The solu-
tion in H was then forced into chamber A by nitrogen introduced
through stopcock C and in this way chamber A was rinsed and
the transfer of hydroxide made quantitative. After five such
transfers, the titration was resumed using the small generating
cathode, D in Figure 2, and the 0.643 mamp. output of the
constant current source. The titration was completed by pass-
ing current in small increments and measuring the pH of the
solution after each increment. Before each pH measurement
chamber A was rinsed three times with solution from H by using
nitrogen pressure and stopcock C as described.

Sample weights of potassium dichromate were chosen so
that about 20,000 microequivalents were titrated. The number
of coulombs passed in each titration was determined in the
same manner as for reductimetric titrations.

DISCUSSION

Reductimetric Titrations with Electrogenerated Iron(II)

Current efficiency

The conditions for the electrogeneration of iron(II) with one hundred per cent current efficiency from iron(III) in sulfuric acid solution were determined by Marinenko and Taylor (15) who used the method of Lingane and co-workers (12, 13). By the same method the conditions for the one hundred per cent efficient generation of iron(II) in perchloric acid were determined. Figure 3 shows current density versus potential curves for a platinum cathode immersed in a well stirred solution containing iron(III) and perchloric acid. Curve A is for a 4.0 M perchloric acid solution containing no iron(III). The potential of the cathode corresponds to the reduction of hydrogen ion. Curve B is for an identical solution this time containing 0.05 M iron(III). At low current densities, below 2 mamp. per cm², the potential of the cathode corresponds to the reduction of iron(III). However, as the current density increases the potential of the cathode rapidly becomes more negative until curves A and B superimpose indicating the reduction of hydrogen ion and the loss of current efficiency. Curves C, D, and E correspond to increasing iron(III) concentrations. In this work the current density on the cathode never exceeded 2.3 mamp. per cm². The initial iron(III) concentration was 2.0 M. After pregeneration of iron(II) almost

Figure 3.   Current density applied to a platinum cathode
versus the potential of the cathode.   A. 4.0 M
$HClO_4$; B. 0.01 M Fe(III) in 4.0 M $HClO_4$; C. 0.05
M Fe(III) in 4.0 M $HClO_4$; D. 0.10 M Fe(III) in 4.0
M $HClO_4$; E. 0.20 M Fe(III) in 4.0 M $HClO_4$.
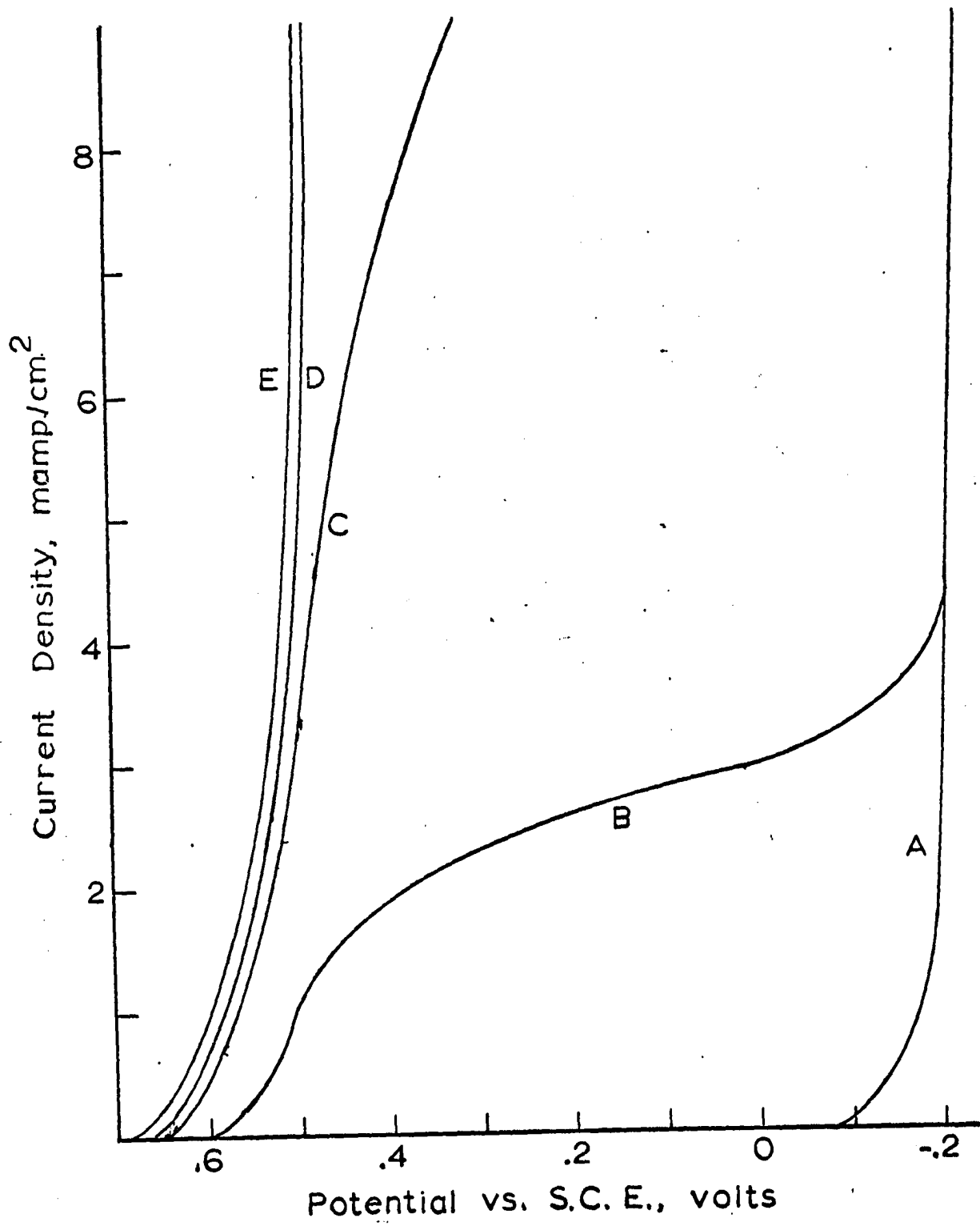
equivalent to one gm. of potassium dichromate or ten gm. of ammonium hexanitratocerate, about 20,000 microequivalents, the concentration of iron(III) dropped to 0.16 M. As can be seen from Figure 3, current efficiency was therefore maintained.

End-point detection

The end-point in the titration of potassium dichromate was determined amperometrically using the electrode pair: s.c.e.-platinum (bright foil, 1 cm^2 total area). The platinum electrode was made 0.875 volts positive to the s.c.e. using a Leeds and Northrup Company Electrochemograph. At this potential dichromate is not reduced owing to the irreversibility of the dichromate-chromic couple and no cathodic current flows before the end-point; iron(II) is oxidized, however, and the end-point is marked by the first current flow as indicated by the microammeter on the polarograph.

The end-point in a titration of dichromate is shown in Figure 4. The end-point could easily be determined to the nearest one-tenth microequivalent. Inasmuch as one gram of potassium dichromate contains about 20,000 microequivalents, the end-point was easily determined to the desired accuracy of one part in 100,000.

The end-point detection system used in the titration of dichromate could not be used in titration of cerium(IV) with electrogenerated iron(II). At the applied potentials required to oxidize iron(II), cerium(IV) is reduced. A cathodic current, resulting from the reduction the cerium(IV) flows before the

Figure 4. End-point in the titration of potassium dichromate
with electrogenerated iron(II). Indicating
electrode system: 0.875 v. vs. s.c.e. applied to
a platinum foil 1 cm^2 in this area.

Fe(II) Generated, uequiv.
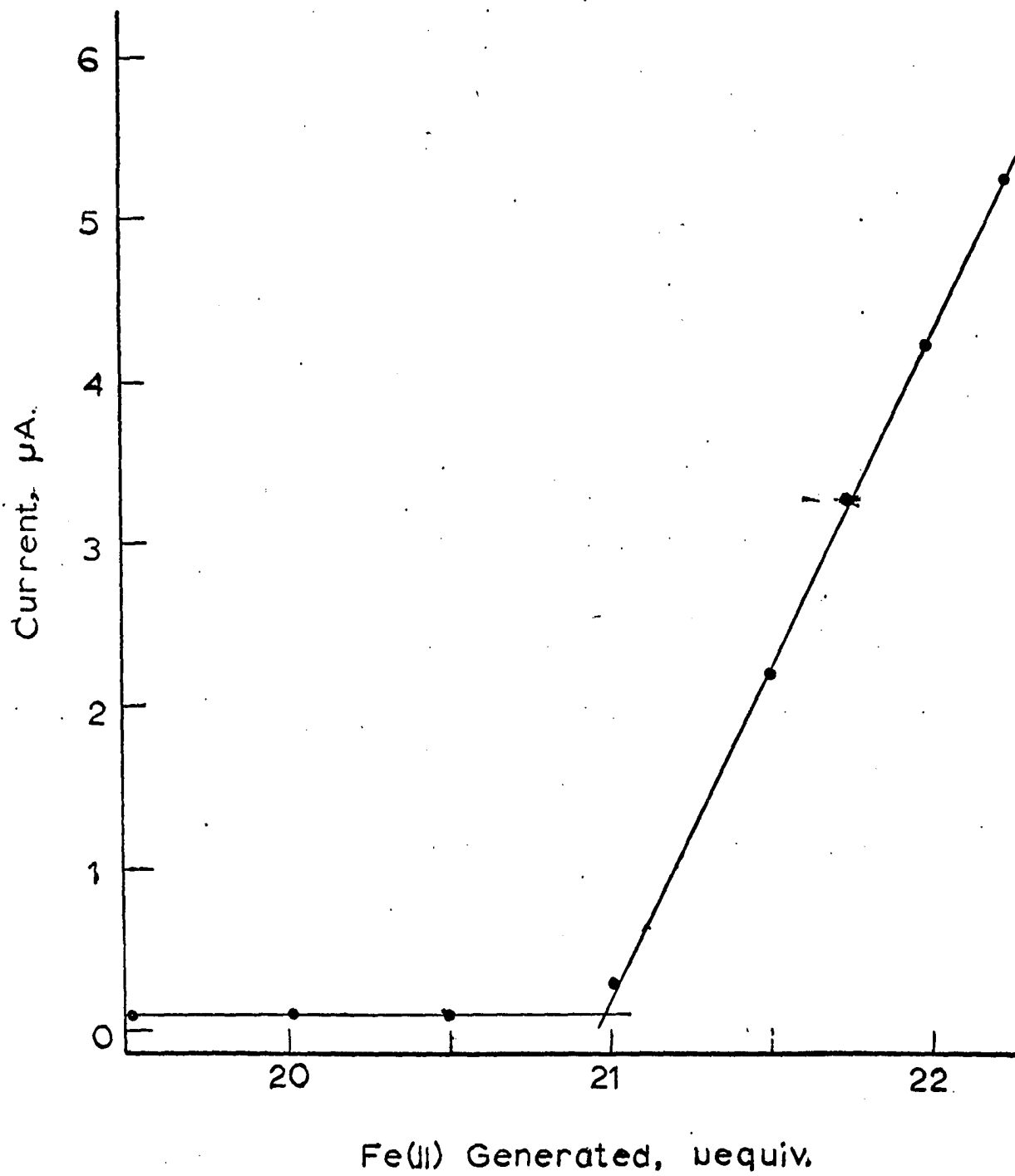
end-point, and an anodic current due to the oxidation of iron(II) flows after the end-point. The microammeter records a continuous increase in current and the change from cathodic current to anodic current at the end-point is difficult to locate.

The end-point detection system used in the titration of cerium(IV) was that of Stone and Scholten (26). A potential of 100 mv. was applied to two platinum electrodes, each 1.0 cm^2 in total surface area, using a Leeds and Northrup Type E Electrochemograph to supply the potential and measure the current. The current before the equivalence-point accompanying the reduction of cerium(IV) decreased as the concentration of cerium(IV) decreased; beyond the equivalent-point the current accompanying the oxidation of the iron(II) formed increased with increasing iron(II). A typical end-point is shown in Figure 5. The current fell to zero and remained at zero for about two microequivalents before increasing. The equivalence-point was taken at point A, Figure 5, the point at which a definite increase in the current was observed, and this point was used in both the pretitration and the titration proper.

As discussed in the next paragraph, the horizontal portion of the indicating current is caused by the reduction of platinum oxide on the surface of the indicating electrodes, this platinum oxide being formed just prior to the end-point by

Figure 5. End-point in the titration of ammonium hexanitratocerate with electro-
generated iron(II). Indicating electrode system: 100 mv. applied to
two platinum foil electrodes, each 1 cm^2 in area.
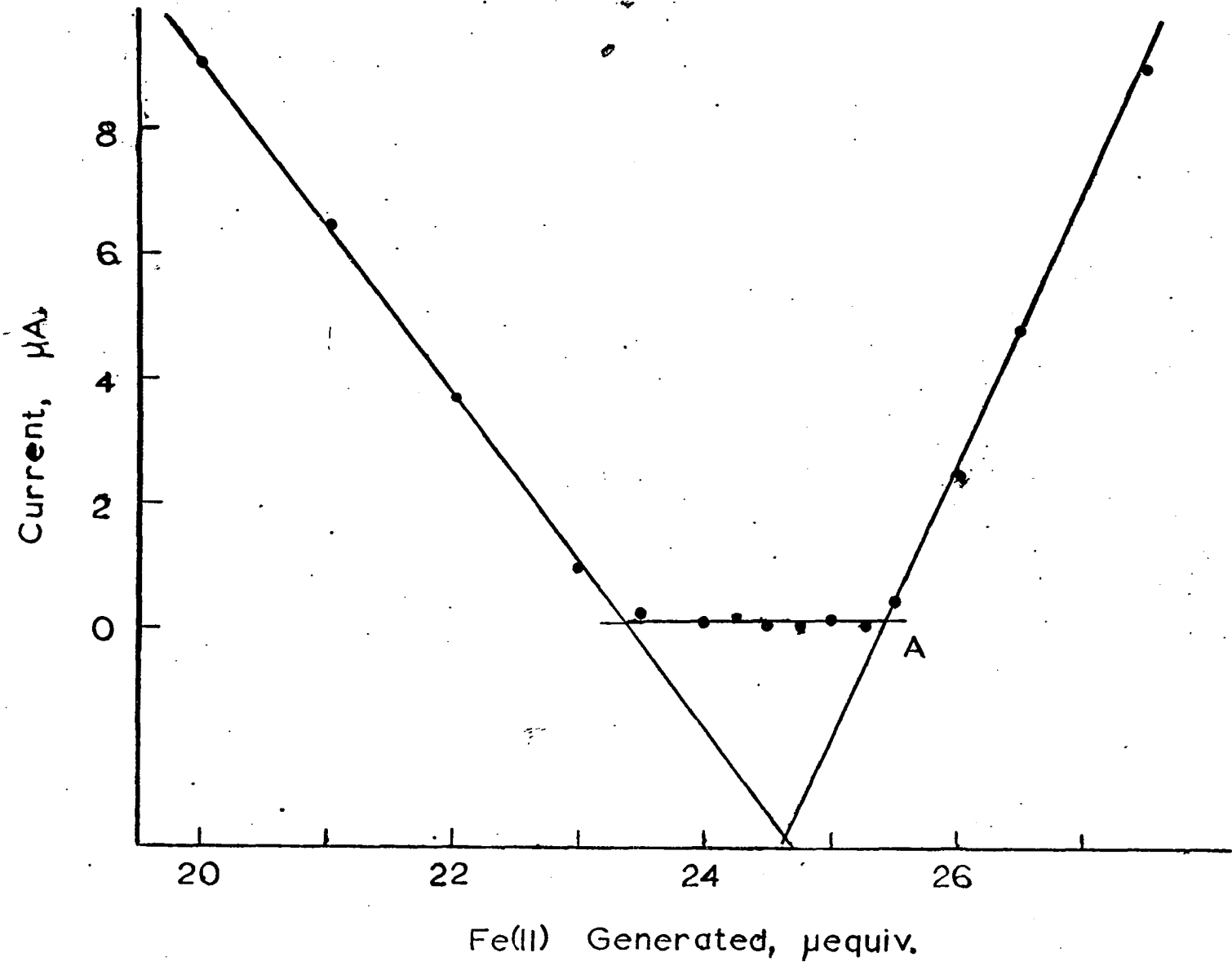
attack of the platinum by cerium(IV). It was hoped that the extent of formation and removal of this platinum oxide was the same in the two end-points used in each analysis. However, as will be seen in the results reported in Table 1 and 4, the standard deviation in the analysis of the ammonium hexanitratocerate is 2 to 2.5 times that of the analysis of the potassium dichromate and this probably results from the uncertainty in the end-point.

Platinum oxide formation as a complication in end-point detection

The existence of films of finely divided metallic platinum and of platinum oxide on bright platinum surfaces has been demonstrated by various workers, in particular by Ross and Shain (19), by Kolthoff and Nightingale (9), by Anson (1,2), and by Lee, Adams and Bricker (11). In substance, these papers report that the surface of bright platinum is oxidized to platinous oxide by various strong oxidizing agents and the oxide reduced by iron(II) or iodide. Ross and Shain showed how this formation of oxide introduces an error into the titration of dichromate with iron(II) by delaying the potentiometric end-point, the size of the error, depending on the direction of titration is governed by the speeds of formation and reduction of the oxide.

Some further experiments were made to confirm that the anomalous end-point behavior observed in this work actually

resulted from oxidation of the platinum indicating electrodes. It was found that the plateau observed at the end-point was extended by immersing the electrodes in a solution of cerium-(IV) before using them in a titration; the plateau was reduced (to one microequivalent) by immersing the electrodes in iron(II) sulfate, rinsing and immediately using them in a titration already close to the end-point. Reduction in the area of the electrode resulted in a reduction of the length of the plateau; however, this is not a solution to the problem for the indicator current passed is also decreased and the lower slopes render the end-point less certain. Annealing the platinum foils before use and mounting them gently to avoid introducing surface strains or work hardening gave electrodes which did not function at all for a minute or so, the indicating current fluctuating widely but finally settling down and displaying the usual plateau; this surprising result indicates that the platinum oxide-platinum couple must be present for current flow, such a result being implicit in the work of Lee, Adams and Bricker (11).

The length of the plateau observed, 2 microequivalents in Figure 5, makes it possible to calculate the amount of platinum oxidized: 195 μg.; taking the atomic radius of platinum at 1.29 Å and assuming a simple structure of eight platinum atoms at the corners of a cube, calculation indicates the platinum reacting to form oxide to be about 50 atoms deep.

Because of the length of the plateau depends on the previous mechanical and chemical treatment given the electrode, an empirical approach to the problem was about all that could be made. The conditions prior to the end-point in the pretitration and in the actual titration were made as identical as possible. Point A of Figure 5 was taken as the end-point on the assumption that all platinum(II) was reduced at this point in the pretitration and in the actual titration. Any platinum oxidized during the titration being at the expense of cerium(IV), and an equivalent number of coulombs were presumably required to reduce the oxidized platinum so that in effect only cerium(IV) was titrated.

Comment on sequence adopted during titration

The pretitration procedure was used to insure that all iron in solution was present as iron(III), except for that generated beyond the end-point which was measured and taken into account in the calculations. Any other oxidizable or reducible impurities were presumably removed also by the pretitrations. Immediately after the pretitration the platinum indicating electrodes were raised above the solution and rinsed with a minimum volume of distilled deaerated water. After the major part of the iron(II) had been generated and the sample added and dissolved, the electrodes were again immersed and the titration completed. In this manner the electrodes were in contact with oxidizing agent for approximately the same

length of time in the pretitration and in the actual titration.

For two reasons, about 99.8 per cent of the iron(II) was generated before the sample was added to the catholyte. 1) The only reaction at the cathode was thus the reduction of iron(III) and the back e.m.f. was thus constant during almost the entire generation and the even slight change in current which might result from a shift from the cerium(IV)-cerium(III) couple to the iron(III)-iron(II) couple was obviated. 2) Reduction of nitrate, added necessarily in the titration of ammonium hexanitratocerate, was avoided. Nitrate is reduced slowly by iron-(II) and, in this work in which titrations extended over eight hours, the interference became serious if the sample were added immediately.

Actually, as shown in the results tabulated in Table 1, identical results were obtained in the analysis of potassium dichromate by adding the sample immediately and by deferring the addition until the iron(II) had been almost completely generated.

Platinum boats were used in the titrations of the potassium dichromate. Although an identical result was obtained in the one analysis in which the sample was carried on a glass boat, it is possible that platinum was being oxidized by the dichromate and reduced by iron(II) as the end-point was approached. Such oxidation and reduction is not detectable in this titration because no current flows in the

indicating system until the end-point is passed. Glass boats were used in the titrations of ammonium hexanitratocerate.

Following the procedure outlined above, a second sample of potassium dichromate was sometimes titrated in the same solution, the end-point in the first titration becoming the pretitration end-point of the second. Titration of a third sample was not feasible owing to precipitation of potassium perchlorate which occluded dichromate to the extent of becoming yellow in color. A second sample of ammonium hexanitratocerate cannot be so titrated because of the reduction of nitrate (in actual trials positive errors of ten per cent).

<center>Neutralization Titrations with Externally</center>

<center>Electrogenerated Hydroxide Ion</center>

Current efficiency

The electrogeneration of hydroxide ion from a sodium perchlorate solution proceeds with 100% current efficiency since there are no species more easily reduced than water present. It is clear from the balanced equations that a hydrogen ion is consumed for every electron used in the reduction of such species as chlorate or perchlorate so that even if traces of chlorate were present or traces of perchlorate were reduced overall current efficiency was maintained.

<u>End-point detection</u>

A plot of pH versus milliliters of titrant for the titra-
tion of potassium dichromate with 0.1 N sodium hydroxide is
shown in Figure 6. It is evident from this plot that the end-
point in coulometric neutralization titrations could be deter-
mined by following the pH of the potassium dichromate solution
during the titration. However, only the final 0.2 per cent
or so of the titration is carried out after the addition of the
sample and, thus, only the last 0.2 per cent of the titration
curve is observed. The actual end-points were calculated by
the differential method of Yan (30) using eight points from
the titration curve which were very near to and bracketed the
end-point. End-points obtained in this way were not so pre-
cise as the amperometric end-points; the estimated error in
the pH end-points being about 0.3 microequivalents.

Figure 6. Titration of 0.9971 grams potassium dichromate with 0.1222 N sodium hydroxide.
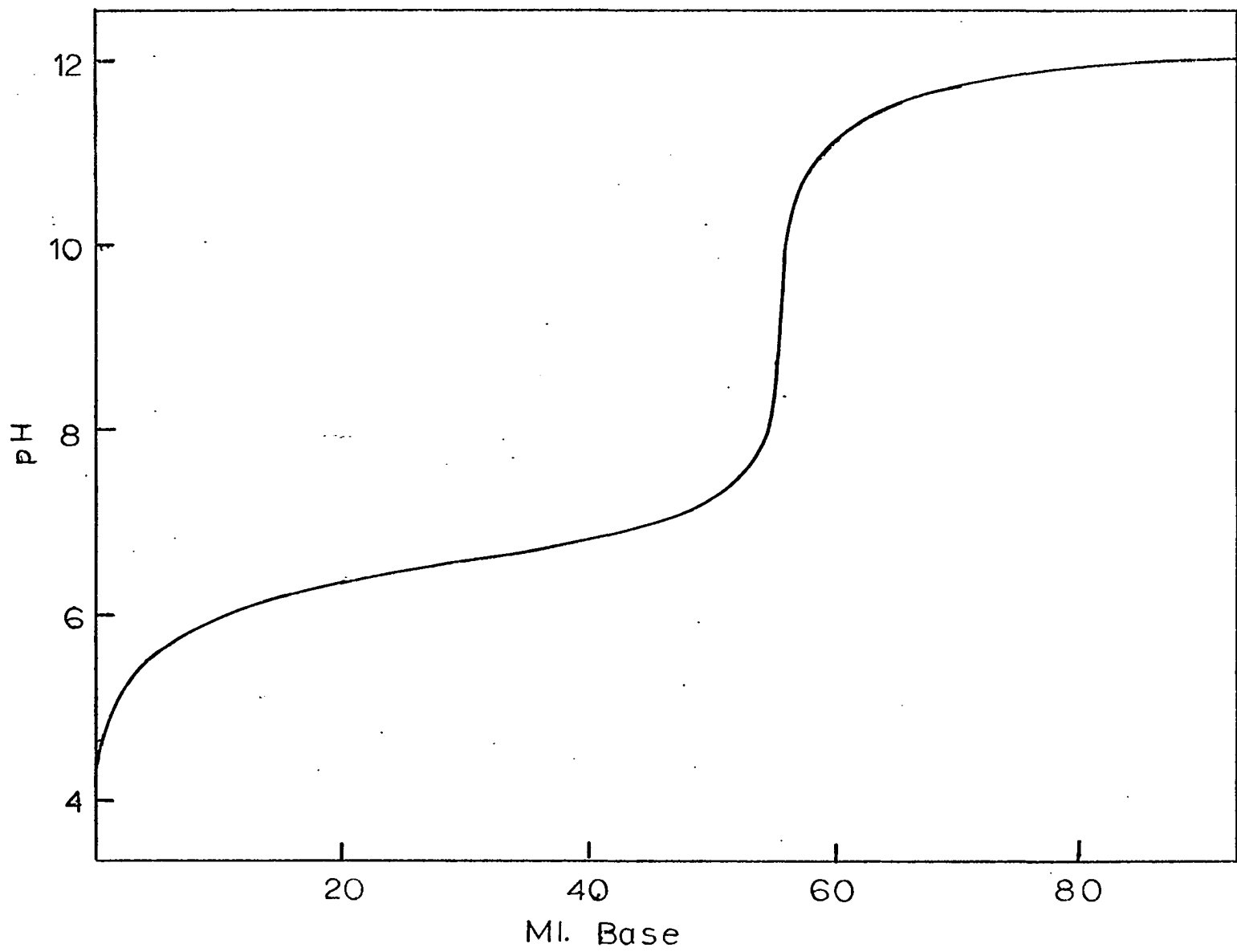
RESULTS

Titrations of Potassium Dichromate

Results of six titrations of NBS 136b, potassium dichromate, with electrogenerated iron(II) are given in Table 1. The average, 99.975 per cent, is in good agreement with the value of 99.977 per cent obtained by Marinenko and Taylor (15), the standard deviation, 0.002, being the same as that of Marinenko and Taylor. This furnishes a check on the calibration of the L and N equipment and on the operation of the cell used. Three of the six titrations were carried out by direct titration, the other three by first generating 99.8 per cent or so of the iron(II) before adding the sample; no difference was detected in the results.

Table 1. Coulometric assay of NBS 136b potassium dichromate by titration with electrogenerated iron(II)

Found per cent	Found in other work per cent	
99.972[a]	99.98	Certificate value
99.974[b]		
99.974[b]	99.977	Marinenko and Taylor (15) coulometric
99.975[a]		
99.977[b]		
99.977[b]		
Average 99.975		
Standard deviation 0.002		

[a]Sample added immediately after pretitration.

[b]Sample added after 99.8 per cent of the iron(II) had been generated.

Results of six titrations of NBS 136b, potassium dichromate, with electrogenerated hydroxide ion are given in Table 2. The average, 99.978 per cent, is in good agreement with the reductimetric titration data. The slightly poorer precision in the neutalization titration data, standard deviation 0.005 per cent, probably reflects a less precise method of end-point detection. The operation of the external generation cell was confirmed by the agreement of neutralization and reductimetric titration data obtained for potassium dichromate and also by titration of potassium acid phthalate. For two titrations of NBS 84d, potassium and phthalate, with electrogenerated hydroxide ion by the same procedure used to titrate the dichromate, purities of 99.986 and 99.990 per cent were obtained. These results are in excellent agreement with the 99.989 per cent purity obtained by Taylor and Smith (28) also by coulometric titration with electrogenerated hydroxide.

Table 2. Coulometric assay of NBS 136b potassium dichromate by titration with electrogenerated hydroxide

Found per cent	
99.970	99.979
99.976	99.980
99.977	99.983
Average	99.978
Standard deviation	0.005

The uncertainties in the atomic weights of potassium, $\pm$ 0.001, chromium, $\pm$ 0.001, and oxygen, $\pm$ 0.0001 introduce an uncertainty of $\pm$ 0.005 in the molecular weight of potassium dichromate (molecular weight, 294.192) or about 1.7 parts in 100,000. The standard deviations of the analysis reported here and of those of Marinenko and Taylor (15) thus approach the uncertainty in the molecular weight of the potassium dichromate. The 0.024 per cent unaccounted for in the coulometric assay must thus result from some impurity and not from errors in the atomic weights.

Svec and Conzemius are reporting (27) from this laboratory a spark source mass spectrographic analysis of NBS 136b for eighty elements excluding the elements in potassium dichromate, and hydrogen, lithium, and the rare gases. The impurities detected and measured semiquantitatively total only 55 p.p.m.s. (parts per million atomic), sodium, rubidium, vanadium and iron accounting for 54 p.p.m.a. A redox equivalent weight was calculated on the assumption that sodium and rubidium replace potassium and that iron and vanadium replace chromium. Thus, for a million atoms of potassium dichromate,

Equivalent weight =

$$\frac{Na_{40}Rb_6K_{((2/11)(10^6)-46)}Cr_{((2/11)(10^6)-8)}V_7Fe_6O_{((7/11)(10^6))}}{3((2/11)(10^6)-8) + 1(7)}$$

$$= \frac{26,744,364}{545,440} = 49.0326$$

the denominator being set up on the assumption that

(2/11)(1,000,000)-8 atoms of chromium undergo a change of oxidation number 3, that 7 atoms of vanadium undergo a change of 1 (vanadium(V) to vanadium(IV)), and that the iron undergoes no change. This value for the equivalent weight departs from the value for pure potassium dichromate, 49.0320, by 1.2 parts in 100,000, less than the standard deviation of 2 parts in 100,000 for the analyses being reported, and also less than the uncertainty resulting from the uncertainties in the atomic weights. Thus, the impurities found do not account for the 240 p.p.m. deficiency in the value obtained by coulometric assay.

The remaining impurity must most certainly be water. A determination of the water in NBS 136μ, potassium dichromate, was made by Schwab and Wichers (21) who found 0.027 and 0.021 per cent water by a vacuum fusion-manometric method. Under the microscope Schwab and Wichers actually observed bubbles in the crystals of NBS 136. Further, Svec and Conzemius (27) found hydride clustering in the pre-spark mass spectrum of NBS 136b indicative of water. We have confirmed by examination with the microscope that bubbles, presumably of mother liquor, are also present in the crystals of NBS 136b. Although the bubbles are not uniformly distributed, presumably the 1-g. samples used were large enough to cancel out the inhomogeneity. It can hardly be an accident, however, that the water in NBS 136 (0.024, the Schwab and Wichers average) and the coulometric assay of NBS 136b, a different lot, (99.976, the

average of Marinenko and Taylor and this work) add up to
100,000. The determination of water in NBS 136b was, there-
fore, undertaken.

A change in the crystalline structure of potassium di-
chromate from triclinic to monoclinic has been reported (8,
22); the transition temperature being about 240°C. Examina-
tion of crystals of potassium dichromate under a polarizing
microscope show that the phase change is accompanied by a
shattering of the crystal. Furthermore, the crystals appeared
to be shattered in a way that indicated the bubbles to be
bursting.

A twenty gram sample of potassium dichromate was dried
for 24 hours at 100°C to remove surface water. After weigh-
ing, the sample was placed in a muffle furnace at 260°C for
48 hours. The weight loss amounted to 0.018 per cent. After
an additional 48 hours the weight loss had increased slightly
to 0.019 per cent. No additional weight loss was found over
the next several days. The weight loss when added to 99.977
per cent, the average of the value of Marinenko and Taylor
and the two independent values obtained in this work, totals
99.996 per cent. The remaining 0.004 per cent may be accounted
for by the impurities or experimental error.

In order to establish that the weight loss at 260°C was
due to the loss of water and not the decomposition of potassium
dichromate, the dried sample was assayed by coulometric titra-
tion with electrogenerated iron(II) as described. The results,

given in Table 3, averaged 100.003 per cent, slightly greater than expected. Although it is fruitless to try to explain the slightly high results, the possibility of decomposition of the potassium dichromate during the extended high temperature drying is not ruled out.

Table 3. Coulometric assay of NBS 136b potassium dichromate by titration with electrogenerated iron(II), sample dried 96 hours at 260°C

Found per cent	
99.998	100.004
100.001	100.006
Average	100.003

Titrations of Ammonium Hexanitratocerate

Results of titrations of seven specimens of ammonium hexanitratocerate are given in Table 4, together with the thorium content as obtained by emission spectroscopy and reported as ammonium hexanitratothorate.

The uncertainties in the atomic weights of nitrogen, $\pm$ 0.00005, hydrogen, $\pm$ 0.00001, and oxygen, $\pm$ 0.0001, are overshadowed by the uncertainty in the atomic weight of cerium, $\pm$ 0.01; thus, for ammonium hexanitratocerate, $CeN_8H_8O_{18}$, molecular weight 548.23, the total uncertainty in the $N_8H_8O_{18}$ portion is $\pm$ 0.0023 and that in the cerium $\pm$ 0.01 or about two parts in 100,000.

Table 4. Coulometric assay and thorium content of various preparations of ammonium hexanitratocerate

Specimen and source	Found per cent	Thorium content as p.p.m. $(NH_4)_2Th(NO_3)_6$	Found in other work per cent
A Certified standard of reference grade[a]	99.965 99.969 99.969 99.972 99.976 99.978	340	99.97 Certified value of G. Frederick Smith Chemical Company[b]
Average	99.972		
Standard deviation	0.005		
B Certified standard of reference grade[a]	99.993 99.990	160	100.00 Certified value of G. Frederick Smith Chemical Company[b]
Average	99.992		
C Prepared from basnaesite	99.980 99.982 99.987 99.988	<40[c]	
Average	99.984		
D Reagent grade[a]	99.959 99.962 99.966	340	
Average	99.962		

[a]G. Frederick Smith Chemical Company, Columbus, Ohio.

[b]As determined by weight buret titration of NBS sodium oxalate.

[c]Thorium content less than the detection limit, 40 p.p.m. ammonium hexanitratothorate.

Table 4. (continued)

Specimen and source		Found per cent	Thorium content as p.p.m. $(NH_4)_2Th(NO_3)_6$	Found in other work per cent
E				
Reagent grade[a]		100.022	140	
		100.026		
		100.030		
	Average	100.026		
F				
Reagent grade[a]		99.433	2,190	
		99.430		
	Average	99.433		
G				
Reagent grade[a]		98.705[d]	7,900	
		98.668[d]		
	Average	98.686		

[d] 1-g. Samples only because of limited amount of material.

The precision of the analyses of ammonium hexanitrato-cerate was somewhat poorer than that of the analysis of the dichromate, the standard deviation being 0.005 (per cent purity). This lower precision undoubtedly resulted from the difficulty in determining the end-point with high precision as discussed above.

The specimens of ammonium hexanitratocerate designated A and B were obtained from the G. Frederick Smith Chemical Company in 1966 and 1967 as "Certified Standard of Reference" materials. The coulometric assays reported check the values of the Smith Company (Table 4), the latter having been obtained (23) by weight buret titrations of NBS arsenic trioxide and reliable probably to two parts in 10,000. The thorium in these samples expressed as ammonium hexanitratothorate added to the coulometric assay values give 100.006 and 100.008, respectively. Examination under the microscope revealed that the crystals of Specimens A and B were small and poorly formed; occasional in-clusions, presumably of mother liquor, were observed but they were far less frequent than in NBS 136b potassium dichromate.

As described above under Experimental Work, the prepara-tion of ammonium hexanitratocerate from the rare earth oxide concentrate from basnaesite was straight forward and easy. The results of analyses of the materials obtained from the fourth and fifth recrystallizations were identical. Although the thorium in Specimen C was below the detection limit of the

emission spectrographic method, the assay, average 99.984, indicated some 156 p.p.m. of impurity present. Even so, this simple preparation is equal in purity to NBS 136b potassium dichromate and equally acceptable as a primary standard.

Specimens D, E, F and G were "Reagent Grade" materials, no claim having been made by the manufacturer that they could be used as primary standard materials. Specimens D and E are sufficiently pure to serve well as primary standard material but the lack of information as to the extent of the purification steps used makes it idle to speculate about them, although such speculation about E is especially inviting because of the high assay value together with appreciable thorium. Specimens F and G contain relatively large amounts of thorium and it is apparent that the oxidizing capacity falls off with increasing content of thorium as expected.

Because of recent advances in the technology of the rare earths, starting materials essentially free of thorium are now available commercially and future commercial preparations of ammonium hexanitratocerate should be essentially thorium-free even without the numerous recrystallizations now known to be necessary for the elimination of thorium (25). The present work leaves no doubt that ammonium hexanitratocerate is an excellent primary standard.

SUMMARY

A high precision assay of the primary standards potassium dichromate and ammonium hexanitratocerate has been carried out by the coulometric method.

High precision coulometric titration apparatus was assembled largely from commercial sources: constant current source, standard resistance, and standard voltage, Leeds and Northrup Company, standard frequency oscillator, American Time Products, Inc., weights, Wm. Ainsworth and Sons, Inc., calibrated at the National Bureau of Standards. Apparatus was housed in a constant temperature room and frequent checks were made that all calibrations remained constant.

Two coulometric cells have been designed, one for the internal generation of iron(II), used to titrate the oxidizing agents potassium dichromate and ammonium hexanitratocerate, and a second for the external generation of sodium hydroxide, used for the titration of potassium dichromate as an acid and potassium acid phthalate.

The anode and cathode compartments of both cells are separated by two ultrafine glass frits and an intermediate electrolyte compartment to insure separation of anode and cathode electrolysis products.

The external generation cell, designed for the analysis of materials which undergo undesirable electrode reactions, consists of two chambers. The bulk of the titrant is generated

in one chamber, the titrant is brought in contact with the sample in the second chamber, and the titration completed by generating the final small amount of titrant at a second external electrode.

Considerable attention was devoted to proving that these cells operate with one hundred per cent efficiency.

Particular attention has been paid to the problem of end-point detection. End-points in titrations of potassium dichromate with electrogenerated iron(II) were detected amperometrically with one polarized platinum electrode. End-points in the ammonium hexanitratocerate titrations were detected amperometrically using two polarized platinum electrodes. The problem of formation of platinum oxide on the indicating electrodes in the titration of cerium(IV) has been investigated in some detail.

Titrations of six samples of NBS 136b potassium dichromate with electrogenerated iron(II) has given for the purity of this material 99.975 per cent with a standard deviation of 0.002 per cent.

Titration of six samples of NBS 136b potassium dichromate with electrogenerated hydroxide ion has given for the purity of this compound 99.978 per cent with a standard deviation of 0.005 per cent.

It has been shown that NBS 136b potassium dichromate, when heated at 240°C for one week, loses 0.019 per cent in weight with the shattering of the crystals and the loss of

occluded water. Assay by titration with electrogenerated iron(II) of the material so dried has given for the purity ·100.003 with a standard deviation of 0.003 per cent.

Titrations of several preparations of ammonium hexanitratocerate with electrogenerated iron(II) has shown that the oxidizing capacity of this compound·falls off with increasing thorium content. However, the analysis of three preparations, low in thorium, averaged 99.978, 99.984, and 99.992 per cent respectively with standard deviations of 0.005 per cent. Low thorium preparations of ammonium hexanitratocerate are, therefore, the equal of potassium dichromate for use as a primary standard.

LITERATURE CITED

1. Anson, F. C., Anal. Chem., 33, 934 (1961).

2. Anson, F. C., Anal. Chem., 33, 939 (1961).

3. Cooper, F. A. and Quayle, J. C., Analyst, 91, 363 (1963).

4. Craig, D. N., Hoffman, J. I., Law, C. A., and Hamer, W. J., J. Res. Natl. Bur. Std., 64A, 381 (1960).

5. Eckfeldt, E. L. and Shaffer, E. W., Jr., Anal. Chem., 37, 1534 (1965).

6. Fassel, V. A., Jasinski, E. L., Dekalb, E. L., and Lucas, W. V., Anal. Chem., 40, 321 (1968).

7. International Commission on Atomic Weights, J. Am. Chem. Soc., 84, 4175 (1962).

8. Klement, U., Naturwissenschaften, 45, 83 (1958).

9. Kolthoff, I. M. and Nightingale, E. R., Jr., Anal. Chim. Acta, 17, 329 (1957).

10. Kolthoff, I. M. and Vogelenzang, E. H., Rec. trav. chim., 40, 681 (1921).

11. Lee, J. K., Adams, R. N., and Bricker, C. E., Anal. Chim. Acta, 17, 321 (1957).

12. Lingane, J. J. and Anson, F. C., Anal. Chim. Acta, 16, 165 (1956).

13. Lingane, J. J. and Kennady, J. H., Anal. Chim. Acta, 15, 465 (1956).

14. Marinenko, G. and Taylor, J. K., J. Res. Natl. Bur. Std., 67A, 31 (1963).

15. Marinenko, G. and Taylor, J. K., J. Res. Natl. Bur. Std., 67A, 453 (1963).

16. Marinenko, G. and Taylor, J. K., Anal. Chem., 39, 1568 (1967).

17. Meites, L. and Meites, T., Anal. Chem., 20, 984 (1948).

18. Richter, M., Z. Anal. Chem., 21, 204 (1882).

19. Ross, J. W. and Shain, I., Anal. Chem., 28, 548 (1956).

20. Salutsky, M. L., Kirby, H. W., and Quill, L. L., Anal. Chem., 27, 1960 (1955).

21. Schwab, F. W. and Wichers, E., J. Res. Natl. Bur. Std., 33, 121 (1944).

22. Schwab, G. M. and Schwab-Agallidis, E., Naturwissenschaften, 29, 134 (1941).

23. Smith, G. F., Talanta, 14, 1131 (1967).

24. Smith, G. F. and Fly, W. H., Anal. Chem., 21, 1233 (1949).

25. Smith, G. F., Sullivan, V. R., and Frank, G., Ind. Eng. Chem., Anal. Ed., 8, 449 (1936).

26. Stone, K. G. and Scholten, H. G., Anal. Chem., 24, 671 (1952).

27. Svec, H. J. and Conzemius, R. J., to be published in Anal. Chem., ca. 1968.

28. Taylor, J. K. and Smith, S. W., J. Res. Natl. Bur. Std., 63A, 153 (1959).

29. Tutundzic, P. S., Anal. Chim. Acta, 18, 60 (1958).

30. Yan, J. F., Anal. Chem., 37, 1588 (1965).

ACKNOWLEDGEMENT