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Variability in the Standardization of Ceric Sulfate Solution for the Titration of Plutonium

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by

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VARIABILITY IN THE STANDARDIZATION OF CERIC SULFATE SOLUTION FOR THE TITRATION OF PLUTONIUM

by

Glenn R. Waterbury, Dale C. Croley, Charles F. Metz

ABSTRACT

The titer for a ceric sulfate solution was 0.2% lower using sodium oxalate as a standard than when using either arsenic trioxide or plutonium metal standards. Difficulty in standardizing ceric sulfate solutions has been experienced infrequently in the past and has seemed to be associated with a very few lots of ceric sulfate reagent solution. The differences in titers emphasized the fact that the standard material should be similar to the samples to be analyzed. The potential user of ceric sulfate should be alerted to this possible, though rare, error in standardization.

INTRODUCTION

The standardization of ceric sulfate solution using sodium oxalate as the primary standard has been for years a routine operation in this laboratory. With few exceptions, several years of experience showed this standardization to be reliable. The titer of the ceric sulfate solution was equal to the value obtained using a high-purity plutonium metal standard in almost all cases. The accidental discovery that occasionally a particular lot of a commercially available reagent grade ceric sulfate solution did not show the same oxidizing capacity toward commonly used and acceptable primary standards gave rise to investigation into the possible causes. This erratic behavior, although rarely observed, was sufficiently pronounced to cause significant differences in the titer of the ceric sulfate standard solution, particularly in high precision oxidation-reduction titrations.

Although the exact causes were not determined in this limited investigation, this situation is being brought to the attention of those who normally use ceric sulfate standard solutions in quantitative analysis.

REAGENTS

Arsenic trioxide, National Bureau of Standards, Standard Sample 83 C, dated September 11, 1957, 99.99% pure on the basis of effective reducing power, dried at 105°C.

Ceric sulfate solution, approximately $0.5\underline{N}$, in $2\underline{N}$ sulfuric acid, obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. Lots B3 and C1 were used. The lot B3 reagent, as received, contained approximately a 1-inch depth of solids on the bottom of each bottle. Prolonged heating of the mixture, followed by dilution to larger volume, as recommended by the vendor, apparently dissolved the solids. There was no evidence of solids in lot C1.

Ceric sulfate solution, approximately 0.045N, prepared by filtering 1.8 liters of the 0.5N ceric sulfate solution through a medium glass frit and diluting the filtered solution to 20 liters with 450 ml of 36N sulfuric acid and distilled water. The solution was mixed thoroughly by bubbling filtered air through it for several days and then stored in a glass bottle that was painted black to exclude light. The inlet tube of the bottle was connected to a small gas-washing bottle partially filled with ceric sulfate solution of about the same concentration (0.045N). Two solutions, designated 1 and 2 in this report, were prepared; solution 1 was made from lot B3 and solution 2 from lot C1 of 0.5N ceric sulfate solution. Portions of solutions 1 and 2 were evaporated to dryness, the residues were ignited at 950°C, and the ignited salts were spectrographically analyzed. The impurities found in significant concentration are listed in Table I.

Table I
Main Impurities Found in Ceric Sulfate Solutions
(Spectrographic Analyses)

Element	Concentration, %	
	Solution 1, Lot B3	Solution 2, Lot C1
Na	0.03	0.02
Ca	0.1 to 1	0.1
Mn	0.04	0.01
Fe	0.06	0.03
Y	0.3	0.05
La	1 to 10	0.2
Pr	0.1 to 1	0.05
Nd	1 to 10	0.3
Sm	0.1 to 1	0.03
Eu	0.01	< 0.01
Gd	1 to 10	0.03
Tb	0.05	< 0.03
Dy	0.15	0.01
Yb	0.05	< 0.01
Pb	0.04	0.02
Th	0.1	0.1

Plutonium metal, similar to National Bureau of Standards, Standard Sample 949b, 99.99% plutonium. Two lots, designated lot A and lot B, were used.

Sodium oxalate, National Bureau of Standards, Standard Sample 40G, 99.95% effective purity, dried at 105°C. A bottle dated January 26, 1967, was designated Bottle A in this work; one dated April 16, 1962, Bottle B; and one dated November 25, 1966, Bottle C.

PROCEDURES FOR THE STANDARDIZATION OF THE CERIC SULFATE SOLUTION

A. Sodium Oxalate Standard(2)

Accurately weighed solution aliquots containing about 80 *mg* of sodium oxalate dissolved in water were titrated at 75 to 80°C with the ceric sulfate solution added from a weight buret. The endpoint was detected potentiometrically using saturated calomel-platinum electrodes. The titer in milligrams of plutonium per gram of ceric sulfate solution was calculated.

B. Arsenic Trioxide Standard(3)

Accurately weighed portions of the dried standard were dissolved in sodium hydroxide, and the solutions were acidified with sulfuric acid. Osmium tetroxide catalyst and 1,10-phenanthroline ferrous sulfate (ferroin) indicator were added, and the titration was made with ceric sulfate solution added from a weight buret.

C. Plutonium Metal Standard(1)

The metal was dissolved in 3N hydrochloric acid, and weighed aliquots containing about 25 *mg* of plutonium were fumed repeatedly with sulfuric acid. The plutonium was reduced to the (III) oxidation state with zinc amalgam, then oxidized to plutonium(IV) with the ceric sulfate solution added from a weight buret. The endpoint was detected potentiometrically using saturated calomel-platinum electrodes.

RESULTS AND DISCUSSION

Standardizations of ceric sulfate solution 1, prepared from lot B3 of the concentrated reagent solution, were performed repeatedly from March 16 to May 29, 1967 (see Table II). The first three standardizations were against sodium oxalate from Bottle A of lot 40G; Bottle B was used for the fourth standardization, and Bottle C for the eighth series of titrations. Arsenic trioxide, lot 83 C, was the fifth and ninth standard material; plutonium metal (lot A) was the sixth standard, and (lot B) was used in the seventh standardization. Bottle B of the sodium oxalate was again the standard for the tenth set of titrations, which followed its use without difficulty in the standardizations of ceric sulfate solution 2. The results in Table II show that standardizations against sodium oxalate from each of the three bottles gave a titer that was about 0.23% lower than that obtained using either plutonium metal or arsenic trioxide standards.

A portion of ceric sulfate solution 1 was then filtered through a fine-porosity glass frit, and the filtered solution was standardized against sodium oxalate and arsenic trioxide three additional times. The filtration did not eliminate the difference among the titers obtained. The possibility that suspended insoluble material in the solution was causing the difference in titers seemed unlikely.

Although the cause for the difference in titers was unknown, the reproducibility of the results using sodium oxalate standards from different bottles strongly suggests that the standard salt was not contaminated. It seems more likely that the ceric sulfate reagent was at fault. Perhaps some material in the ceric sulfate reagent did not oxidize oxalate rapidly at 75°C but did oxidize either arsenic trioxide or plutonium(III). This supposition gained further support from the data obtained for ceric sulfate solution 2 prepared on May 8, 1967, from lot C1 of 0.5N ceric sulfate solution. This solution was allowed to stand three weeks and then standardized using sodium oxalate, lot 40 G (Bottle B); arsenic trioxide, lot 83 C; and plutonium metal, lot A, as standards (Table III). The results show that equal titers were obtained for this ceric sulfate solution using either sodium oxalate, arsenic trioxide, or plutonium metal standards.

The concentrations of impurities in solution 1 were significantly higher than in solution 2, but the elements found were not suspected of causing a negative bias in the standardization using sodium oxalate standard. Although the data were not adequate to show the causes for the differences obtained in the standardizations of ceric sulfate solution 1, there was no doubt of the magnitude of the error in the titer. The quality of solution 1, and therefore of the 0.5N stock solution, lot B3, was quite suspect, and the reagent was withdrawn from use. These results pointed out again the fact that the best standard material is the one most similar to the sample to be analyzed, in this case plutonium. The frequent checking of the titer of the ceric sulfate solutions by titrating samples of high purity plutonium will be continued.

ACKNOWLEDGMENTS

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Table II

Standardization of Ceric Sulfate Solution 1

Number	Titration Date	Standard	Date on Bottle	Pu Titer, mg Pu/g	Av. Pu Titer, mg Pu/g
1	3-16-67	Sodium oxalate, 40 G Bottle A	1-26-61	8.517, 8.522, 8.524, 8.525, 8.523, 8.523	8.522
2	4-10-67	Sodium oxalate, 40 G Bottle A	1-26-61	8.519, 8.522, 8.519, 8.520, 8.520, 8.522	8.520
3	4-11-67	Sodium oxalate, 40 G Bottle A	1-26-61	8.521, 8.517 8.520	8.519
4	4-12-67	Sodium oxalate, 40 G Bottle B	4-16-62	8.524, 8.521 8.519	8.521
5	4-13-67	Arsenic trioxide, 83 C	9-11-57	8.541, 8.541, 8.542, 8.542	8.541
6	4-14-67	Pu metal lot A		8.538, 8.537, 8.538, 8.543 8.544, 8.543, 8.541	8.540
7	4-14-67	Pu metal lot B		8.538, 8.541	8.540
8	5-9-67	Sodium oxalate, 40 G Bottle C[a]	11-25-66	8.520, 8.520	8.520
9	5-11-67	Arsenic trioxide, 83 C	9-11-57	8.539, 8.544, 8.544, 8.542	8.542
10	5-29-67	Sodium oxalate, 40 G Bottle B	4-16-62	8.519, 8.518	8.519

[a] This standardization performed using sodium oxalate from a special shipment from the National Bureau of Standards.

Table III

Standardization of Ceric Sulfate Solution 2

Titration Date	Standard	Pu Titer mg Pu/g	Av. Pu Titer, mg Pu/g
5-29-67	Sodium oxalate, 40 G, Bottle B	11.027, 11.028, 11.028, 11.029	11.028
5-31-67	Arsenic trioxide 83 C	11.028, 11.024 11.027, 11.028	11.027
7-5-67	Plutonium metal, lot A	11.029, 11.026, 11.024, 11.024	11.026
7-18-67	Arsenic trioxide, 83 C	11.026, 11.026, 11.027, 11.028, 11.029, 11.029	11.028