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DETERMINATION OF VALENCE STATES OF IRON IN GLASS AND OF URANIUM IN CALCIUM FLUORIDE SINGLE CRYSTALS

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DETERMINATION OF VALENCE STATES OF IRON IN GLASS AND OF URANIUM IN CALCIUM FLUORIDE SINGLE CRYSTALS*

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ABSTRACT

The instantaneous oxidation of macro and semi-micro amounts of ferrous iron in various types of glasses; of ferrous iron in magnesium oxide; and of semi-micro quantities of uranium(III), respectively uranium(IV) in calcium fluoride single crystals by excess cerate which is present in the solvent system, followed by a ferrous ammonium sulfate backtritration, is the basis for a simple, accurate method which, furthermore, obviates the need for an inert atmosphere. Formal oxidation potentials of the Ce(IV)/Ce(III) couple and the Fe(III)/Fe(II) couple in the hydrofluoric-sulfuric acid glass-dissolving mixture were estimated.

*This work was performed under the auspices of the U.S. Atomic Energy Commission.

INTRODUCTION

As the result of studies in this laboratory, it became necessary to determine the ferrous and ferric oxide content of sodium disilicate glasses which had been used in high temperature electrochemistry experiments. A wealth of publications deals with the determination of iron(II). Among others, K.L. Cheng (1) discusses various methods for the determination of ferrous oxide in some solids and, stating the limitations for his purpose, developed a procedure for determining ferrous iron in ferrites. However, his approach is unsuitable for the decomposition of glass. A method described by P. Close et al. (2) for the ferrous analysis in glass was selected. They recommend a hydrofluoric-sulfuric acid mixture for the dissolution of glass under an inert atmosphere, followed by a cerate titration of the liberated ferrous ion. The ferrous results obtained by this procedure in our laboratory were widely scattered, and our attempt to modify the method did not improve the precision.

The method presented here is based upon the fact that the cerate ion is stable for an extended period over the temperature range from 20°C to 100°C in the hydrofluoric-sulfuric acid mixture. This permits the instantaneous oxidation of the released ferrous ion by a known excess of standard cerate during the dissolution of the glass and thus obviates the need for an inert atmosphere. The results obtained on glass samples by this procedure are precise and the accuracy of the determination on simulated samples was within 1%. The method is also applicable to the determination of ferrous oxide in magnesium oxide. The formal oxidation potentials for the ceric-cerous couple and for the ferric-ferrous couple are estimated in the glass-dissolving acid mixture and their importance is discussed. The procedure was further employed in

determining valence states of semi-micro quantities of uranium in calcium fluoride single crystals.

EXPERIMENTAL

Apparatus. Thirty milliliter Teflon beakers with pouring lips, 3.4 cm o.d., 2.7 cm i.d., and 4.6 cm high were machined from commercial rod stock and were fitted with Teflon covers. Teflon covered magnetic stirring bars, in conjunction with Mag-Mix magnetic stirrers were used to agitate the glass-acid mixtures. Micro washout pipets, guaranteed "to contain" within ±0.01% of the stated volume, were used to aliquot the standard solutions and the indicator. Hydrofluoric acid was aliquoted with 2.0 ml plastic pipets. A previously described lead column reductor was used in determining the total uranium (3) and the total iron (4). The potential measurements were made with a Digi-Tec digital DC voltmeter.

Reagents. All chemicals used were reagent grade unless otherwise specified. Sufficient ceric ammonium nitrate was dissolved in sulfuric acid to give, on final dilution, a stock solution 0.1M in cerate and 1M in sulfuric acid. One-hundredth molar cerate solutions were prepared by dilution of the stock solution while maintaining a sulfuric acid concentration of 10% by volume. The 0.1M solution was stable for at least two years, and the 0.01M dilution was stable for at least three weeks. A standard 0.001M ferrous ammonium sulfate solution, 10% by volume in sulfuric acid, was prepared daily by direct weighing. Sufficient iron wire for standardization was dissolved with hydrochloric acid to give a solution of 0.1M iron(III) on dilution. A 1:20 dilution of the commercially available 1,10 (ortho)-phenanthroline ferrous

sulfate (Ferroin) indicator, 0.025M, from G.F. Smith Chemical Company was employed. Concentrated sulfuric acid and 48% hydrofluoric acid were purified with permanganate as described previously (2) and were used throughout the procedure for iron. N.B.S. uranium dioxide, 0.1M ferric sulfate solution, and a calcium fluoride single crystal were used in the uranium determination.

Potential Measurements. The formal oxidation potential measurements of the ceric-cerous couple were conducted in a 100 ml polyethylene cell, using a platinum wire and a Lingane type saturated calomel electrode (SCE) combination. Diffusion of the potassium chloride into the cell and contact of the glass electrode with hydrofluoric acid is not desirable, therefore the electrical contact through the cell was accomplished by allowing the SCE bridge to dip into a 5M ammonium nitrate solution, and by bridging from there into the cell by a bees' wax-coated U-tube having an upturned tip. The agar-agar salt bridge was avoided because strong oxidants are known to attack it (5). The entire cell and associated parts were immersed in a 25.0° ± 0.1°C constant temperature bath.

The solution used consisted of 1.00 ml of 0.0992M ceric ion and 1.00 ml of 0.0992M cerous ion, both in 1M sulfuric acid, 10 ml of hydrofluoric acid, 10 ml of sulfuric acid, and 20 ml of water. The mixture was stirred continuously with a magnetic stirrer while potential measurements were made at 5 min intervals.

The measurement of the ferric-ferrous formal oxidation potential was made in the same cell as described above. In this case the bridge solution was saturated potassium sulfate, since contact of a divalent iron solution with a strong nitrate solution might result in oxidation of the ferrous ion. The ferric-ferrous potential measurement was made on a solution similar to the

one above, but containing 1.00 ml of 0.0988M ferric ion and 1.00 ml of 0.0999M ferrous ion instead of cerium. Prior to aliquoting the iron into the acid-water solution, the mixture was purged of oxygen with a chip of Dry Ice. Carbon dioxide gas was directed over the surface of the solution during the time the potential measurements were made.

Recommended Procedures - Standardization of 0.01M Ceric Sulfate: Deliver a 3 ml aliquot of the 0.1M standard iron solution into a 30 ml platinum crucible and fume to almost dryness with 1 ml sulfuric acid and 2 ml hydrofluoric acid. Transfer the sample to a 50 ml beaker, add 5 ml of 4M hydrochloric acid, and dilute to 25 ml. Wash the iron through a lead column reductor with six 25 ml portions of 0.8M hydrochloric acid. Receive the eluent in a 500 ml Erlenmeyer flask which contains 10g boric acid and sufficient Dry Ice to provide an inert atmosphere throughout the subsequent titration. Aliquot 4 ml of sulfuric acid and 1 ml of 1:20 Ferroin solution into the sample flask. While stirring, titrate with the 0.01M cerate solution to the endpoint. Determine indicator and reagent blanks and apply the appropriate titer corrections to the results.

Determination of Ferrous Iron: Grind a glass sample in a Diamonite mortar to pass a hundred mesh. Weigh 100 mg of the glass to give from 0.4 mg to 1.0 mg ferrous oxide. Transfer the sample to a Teflon beaker and aliquot 2 ml of 0.01M standard cerate solution, 2 ml of hydrofluoric acid, and 1 ml of sulfuric acid into the beaker. Stir the mixture magnetically until the glass is dissolved. Some samples require hot acids to affect dissolution. They may be heated for 24 hours or more in a water bath at 100°C without destroying the oxidant. Blanks are treated similarly. Add 10g boric acid to the dissolved sample and stir an additional 5 minutes. Transfer the sample solution to a

250 ml Erlenmeyer flask and aliquot 4 ml of sulfuric acid and 1 ml of 1:20 Ferroin solution into the sample container. Dilute to 100 ml and while stirring, titrate with standard 0.001M ferrous ammonium sulfate to the endpoint. Up to 10 mg of ferrous oxide can be determined by employing the standard cerate stock solution and a standard 0.01M ferrous ammonium sulfate titrant.

Determination of Total Iron: Weigh 50 mg to 100 mg of the 100 mesh glass sample to give from 0.5 mg to 1.0 mg Fe_2O_3. Transfer the sample to a 30 ml platinum crucible and treat the glass as described above for the standardization of the cerate solution. When the sample is dissolved, proceed with the column reduction. Receive the eluent in a 500 ml Erlenmeyer flask which contains a 2 ml aliquot of the 0.01M standard cerate solution and 10g boric acid. Magnetically stir the cerate-boric acid mixture while receiving the eluent. Add 4 ml of sulfuric acid and 1 ml of 1:20 Ferroin solution. Titrate the excess standard cerate with standard 0.001M ferrous ammonium sulfate to the endpoint. Up to 10 mg of total iron can be determined by employing the standard cerate stock solution and a standard 0.01M ferrous ammonium sulfate titrant.

Valence Determination of Uranium: Grind a calcium fluoride-uranium sample in an agate mortar to pass a hundred mesh. Weigh 100 mg to 200 mg to give 0.1 mg to 1.0 mg of uranium. Weigh 100 mg to 200 mg of a finely ground calcium fluoride single crystal, which serves as part of the blank. Transfer the samples to 250 ml Erlenmeyer flasks and aliquot into each 3 ml of 0.01M standard ceric sulfate solution, 1 ml of ferric sulfate solution and, after the addition of 2.5g boric acid, 1 ml of perchloric acid. Suspend the flasks in a boiling water bath and stir the solutions magnetically. When the samples are dissolved,

dilute them to 150 ml with distilled water, adding an aliquot of 5 ml sulfuric acid and one drop of 0.025M Ferroin indicator. Titrate the excess cerate with standard 0.001M ferrous ammonium sulfate.

An independent determination for total uranium must be made on another portion of the sample in order to calculate the change in valence.

DISCUSSION

Ferrous and Ferric Iron: The instantaneous oxidation of divalent iron released upon dissolution of a glass sample has obvious benefits. However, the strong oxidant selected must be stable with respect to light, time, and temperature, and it must be compatible with the highly acidic glass-dissolving mixture. Dichromate and permanganate proved useless. On the other hand, sulfato cerate, in molar sulfuric acid, is stable to light; it has an excellent, long-term stability, and it can be boiled several hours without decomposition (6 and 7). Also, data obtained in this laboratory indicate that it is stable in the hydrofluoric-sulfuric acid mixture, employed in the recommended procedure, for at least six days at room temperature and for more than 24 hours at 100°C.

When sulfato cerate is added to a solution containing hydrofluoric acid, the familiar yellow disappears. This was unexpected. Apparently fluoride complexes ceric ions and probably decreases the oxidation potential of the system. It was thought, therefore, to be of some value to estimate the formal oxidation potential. A range of values from 0.7 v to 0.9 v was obtained for the oxidation potential of the ceric-cerous couple at 25°C. Several problems were attendant: the cerous fluoride gradually forms a gelatinous precipitate which coats the platinum wire, resulting in varying potential readings. The

potential obtained is not strictly a "formal oxidation potential" since both the oxidized and the reduced forms do not remain in solution. However, the potential obtained is sufficiently positive to oxidize ferrous ion under the same conditions. Addition of 10g boric acid results in dissolution of the cerous fluoride and in a marked increase in potential, up to a stable 1.31 v, due to release of cerate ion by borate-fluoride complexing. Further addition of boric acid does not affect the readings. The value reported here is lower than the commonly stated value of 1.44 v and may indicate some residual cerate-fluoride complexing, although the solution measured is saturated with boric acid. The values presented are not corrected for the junction potential.

The strong fluoro complexing of the ferric ion, but not that of the ferrous ion, is well known. Therefore, the low formal oxidation potential of 0.51 v obtained under the recommended conditions was expected. When the fluoride was masked with boric acid, a potential of 0.62 v was obtained. Since the ferric ion is complexed by sulfate ($\log \beta_2 = 5.2$), the value reported here, although lower than that obtained in 1M sulfuric acid (0.68 v), is acceptable. The oxidation potential of oxygen (1.229 v) is considerably more positive than the values reported for the ferric-ferrous couple in either fluoride or sulfate media and, therefore, oxygen must be excluded.

A study was made to correlate the particle size of a commercial glass with the time required for dissolution, and, to determine whether there was any relationship between the particle size and the iron(II) content found. The glass was ground in a Diamonite mortar and sieved to give >20 mesh, <20 mesh, <48 mesh, <80 mesh, and <100 mesh. Approximately 100 mg of each mesh size was dissolved in duplicate for 150 minutes in the hydrofluoric-sulfuric

acid and cerate mixture to establish the amount of iron(II) present. The dissolution time was then shortened with decreasing particle size. Triplicate and quadruplicate results were secured in most cases. The minimum time required for dissolving the particular glass at hand was: <100 mesh: 10 minutes, <80 mesh: 20 minutes, <48 mesh: 45 minutes, <20 mesh: 100 minutes, >20 mesh: 120 minutes. The Fe(II) content was independent of the length of time of grinding. Evidently, no oxidation of iron(II) occurred during prolonged grinding (5 days) or due to the exposure to air of the finely ground sample, supporting the views of Hillebrand (8) and Densem (9). The average value of 35 completely dissolved samples was 0.374% iron(II), covering the range from 0.355% to 0.391%, with a standard deviation of 0.01%. The basis upon which dissolution was judged to be complete were the values obtained for all mesh sizes after 150 minutes of dissolving. Based on the foregoing findings, sodium disilicate glasses, which had been used in high temperature electrochemistry experiments, were analyzed according to the recommended procedure. Reproducible results are represented by: Sample A, 19.12±0.5% Fe(II) (5 determinations) and, Sample B, 25.90±0.15% Fe(II) (3 determinations).

A potentiometric determination of micro amounts of ferrous iron described in the literature (10) seemed to have several drawbacks; in particular, that the glasses submitted for analysis could not be dissolved within five minutes as could those cited. Our method was therefore tested on the semi-micro scale. Standard glasses are not available and had to be simulated by using iron-free quartz wool and known quantities of standard ferrous ammonium sulfate. The amount of Fe(II) found was within 1% of the amount added, (Table I). Table II illustrates the precision obtained for analysis of industrial glasses containing

1% or less ferrous iron. The analytical data quoted by the manufacturer for ferrous and for total iron were usually lower than the results obtained with the proposed method.

For the determination of total iron, an inert atmosphere was eliminated by receiving the reduced eluent in an excess of standard cerate, which is back-titrated with standard ferrous ammonium sulfate. The titration endpoint could be observed more carefully without the Dry Ice, splashing of the sample solution was avoided and, the solutions did not have to be titrated immediately. The accuracy obtained with a series of simulated samples was within 0.3% of the amount of total iron present.

Furthermore, ratios of Fe(II:III) were determined in magnesium oxide crystals which were used in electron paramagnetic resonance studies. The ratios obtained by the recommended procedure, but omitting hydrofluoric and boric acid, were in good agreement with the theoretical values.

The method applies to glasses and to materials which do not contain reducing substances other than ferrous iron and which can be dissolved at 100°C or less. It should be feasible to determine micro amounts of ferrous iron by a slight modification of the proposed method in which the final titration with ferrous ammonium sulfate is substituted by a spectrophotometric determination of the excess cerate at 350 mμ.

The suggested procedure has the following advantages over existing methods for the FeO determination in glass: 1) better precision, 2) elimination of an inert atmosphere for the ferrous iron as well as for the total iron determination, 3) stability of the oxidant at 100°C, and 4) simplicity of operation with common, inexpensive laboratory equipment. Many samples may be determined simultaneously during one eight-hour working day.

Uranium: The principle of an instantaneous oxidation was applied to the determination of the oxidation state of uranium in calcium fluoride single crystals the properties of which are being studied by optical spectroscopy. These crystals contained 0.1-0.8% of uranium believed to be in the +3, respectively the +4 oxidation state. A ferric iron catalyst was required to hasten the oxidation of uranium(IV) to uranium(VI) by cerate.

Preliminary tests were made with simulated samples, using N.B.S. uranium dioxide and reagent grade calcium fluoride. The reagent blank for 100 mg calcium fluoride, combined with the acids and the indicator used in the recommended procedure, consumed 40% of the added standard cerate. In view of a desired overall accuracy of ±10% in the valence determination, a 40% blank could not be tolerated. Instead, a finely ground calcium fluoride single crystal was used in subsequent work. This crystal was grown from specially purified reagents for optical studies. The value of the blank decreased to 10% of the added standard cerate. It was proven that this blank was not due to the calcium fluoride, but exclusively to the acids and indicaotr.

It has been stated (11) that calcium fluoride can be readily dissolved in hot hydrochloric acid in the presence of fluoride-complexing cations. An investigation showed that hydrochloric acid was not an efficient solvent and, that cerate apparently oxidized chloride to chlorine. Perchloric acid was chosen for the recommended procedure because it dissolved the calcium fluoride crystals within several hours just below 100°C and did not interfere with the oxidant.

Accuracy. The method was applied to simulated samples consisting of a calcium fluoride single crystal to which known quantities of N.B.S. uranium dioxide were added. Approximately 100 mg of calcium fluoride were combined with approximately 2.5 mg of uranium dioxide. The results obtained by titrating the excess cerate were low by an average of 10%. A lead column reduction of known uranium dioxide (2.5mg) - calcium fluoride (100 mg) in perchloric acid, oxidized first to the +6 valence state with hydrogen peroxide, gave a 4% positive error for the determination of total uranium.

A pink, single crystal, consisting of calcium fluoride and uranium in the +3 oxidation state as evidenced by the characteristic color, was analyzed in quadruplicate. The precision was ±0.13%. Not enough material was available to permit the determination of total uranium and therefore, the initial valence could not be confirmed.

A green, single crystal, however, was analyzed for total uranium by two independent methods. Neutron activation analysis in duplicate gave 0.79% and 0.82% uranium. A spectrophotometric determination in duplicate (12) resulted in 0.81% and 0.80% uranium. The determination of the change in oxidation state of the uranium by cerate titration to uranium(VI) gave a value of 2.06 (±5%), indicating the presence of uranium(IV) in the crystal. Table III.

Obviously, the method cannot be used without modification if mixtures of several valences and/or reducing substances are present. Additional investigations of the various oxidation states of uranium in calcium fluoride and in other solid materials are in progress.

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Table 1. Semi-micro Determination

Ferrous Ammonium Sulfate and Quartz Wool

m moles Fe(II)

Added	Found	% Error
0.01003	0.00990	- 1.3
0.01003	0.00995	- 0.8
0.01003	0.00995	- 0.8
0.00501	0.00499	- 0.4
0.00501	0.00504	+ 0.6

Table II. Industrial Glasses

Sample	% Fe(II) quoted	% Fe(II) found	No. of det'ns.	% Std. Dev.	% Range
1	0.281	0.306	8	± 0.002	0.302 - 0.309
2	0.546	0.573	9	± 0.008	0.560 - 0.587
3	0.350	1.19	8	± 0.003	1.17 - 1.26
	% Total Iron				
	quoted	found			
1	0.322	0.424	5	± 0.011	0.413 - 0.442
2	0.588	0.660	4	± 0.020	0.635 - 0.685
3	1.19	1.42	4	± 0.060	1.36 - 1.48

Table III. Semi-micro Determination

Uranium in Calcium Fluoride

m equiv. $\times 10^{-5}$ found	m moles $\times 10^{-5}$ U found	Oxidation change
6.57	3.32 (a)	1.94
6.88	3.44 (a)	2.04
6.92	3.36 (s)	2.05
7.18	3.40 (s)	2.12
7.31		2.16
	av. 3.38	av. 2.06

(a) Neutron Activation Analysis, (s) Spectrophotometry

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