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DETERMINATION OF CORROSION PRODUCTS AND ADDITIVES IN HOMOGENEOUS REACTOR FUEL

III. Polarographic Determination of Iron(III)

A. D. Horton
P. F. Thomason

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A. D. Horton and P. F. Thomason

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0. Abstract

An ion-exchange -- polarographic method was developed for the determination of iron(III) in Homogeneous Reactor fuels. Copper, which interferes, is removed from the fuel by plating it onto a cadmium coil. Iron is oxidized to iron(III) by potassium permanganate, and the iron(III) is separated from interfering metal ions by ion exchange on a Dowex 1 resin column that is in the sulfate form. The iron(III) in the effluent is determined polarographically in 0.5 M sodium citrate solution as supporting electrolyte. A fairly well defined polarographic wave is obtained for the iron(III) $\longrightarrow$ iron(II) reduction at a half-wave potential of approximately -0.15 v. vs. the S.C.E. The relative standard deviation of the data for 2 μg of iron(III) per ml of solution in the polarographic cell was 6.5%; for 10 μg of iron(III) per ml it was 0.6%.

1. Introduction

At the time of this report, Homogeneous Reactor fuel contains 10 g of uranium per liter as uranyl sulfate, 2 g of copper per liter as copper sulfate, and 0.2 to 0.5 g of chromium per liter as chromium trioxide. During the operation cycle of the reactor, other metals enter the solution because of the corrosive effect of radiation and because of the acidity of the fuel. The analytical determination of these contaminant metals is a measure of the corrosion of the metallic components of the reactor system. The determinations of nickel, manganese, copper, zirconium, and chromium(VI) in Homogeneous Reactor fuel are described by Horton et al. in previous reports.[1][2]

Iron(III) is present in the fuel as a product of the corrosion of the stainless steel parts of the reactor system. For the experiments described herein, a synthetic fuel was prepared to simulate Homogeneous Reactor fuel. Besides the uranium and the usual additives, other metals were added to represent average corrosion conditions in the reactor.

2. Summary

A synthetic solution was prepared to simulate as closely as possible the composition of the Homogeneous Reactor fuel as it is at the beginning of normal operation of the reactor. It contained

uranium(VI); the additives, copper(II) and chromium(VI); iron(III), which is the most probable valence state of the soluble iron during the normal operation of the reactor; and the major corrosion products, nickel and cobalt, in amounts equal to or greater than the total iron present. A typical synthetic fuel composition is as follows: uranium as uranyl sulfate, 10 g per liter; copper as cupric sulfate, 2 g per liter; chromium(VI) as potassium chromate, 0.1 g per liter; nickel as nickelous sulfate, 0.1 g per liter; iron as ferric sulfate, 0.1 g per liter; and cobalt as cobaltous sulfate, 0.1 g per liter.

Copper interferes in the polarographic determination of iron(III). Because copper passes through the ion-exchange column with iron(III), it must be removed from the fuel before the ion-exchange isolation of iron(III). This is done by plating the copper onto a cadmium coil. As the copper is removed, uranium(VI) and iron(III) are reduced to uranium(IV) and iron(II), respectively. These metals are reoxidized to uranium(VI) and iron(III) by the addition of a slight excess of potassium permanganate.

Iron(III) is determined by passing the sample of Homogeneous Reactor fuel, from which the copper was removed, through a sulfate-form Dowex 1 resin column and collecting the effluent in a supporting electrolyte that is 0.5 M sodium citrate solution. Uranium(VI), permangante, and other

interfering metal ions are adsorbed by the resin. The polarogram of the iron(III) $\longrightarrow$ iron(II) reduction is obtained at a half-wave potential of -0.15 volt vs. the S.C.E.

Iron(III) in synthetic Homogeneous Reactor fuel has been determined with a relative standard deviation of 6.5% for a concentration of 2 μg of Fe(III) per ml of solution in the polarographic cell and of 0.6% for 10 μg of iron(III) per ml.

Any amount of iron(III) that is soluble in the fuel will be separated quantitatively from a 1-ml fuel sample on a sulfate-form Dowex 1 resin column of 3-ml volume. The lower limit of the polarographic determination is 20 μg of total iron per ml of fuel, which is diluted 1:10 for polarographic analysis.

3. Polarographic Determination of Iron(III)

3.1 Removal of Copper from the Fuel. Copper passes through the sulfate-form Dowex 1 resin column under the same conditions as does iron(III). Copper is removed quantitatively from the fuel by the method of Shults and Thomason,[6] in which a cadmium coil is used to plate out the copper from the fuel. Uranium(VI) and iron(III) are reduced to uranium(IV) and iron(II) by this method. The detailed procedure for removing copper from the fuel is given in Section 7.1.2.

3.2 Separation of Iron(III) from the Fuel. To separate the iron from ions that interfere with its polarographic determination, it must first be reoxidized to iron(III) by the addition of a slight excess of potassium permanganate, and all metals that interfere in the determination must be removed from the sample.

Dowex 1 ion-exchange resin in the sulfate form will not adsorb iron(III) from 0.01 M (or more concentrated) sulfuric acid solutions but will adsorb quantitatively the ions of interfering metals, except copper, from a 0.3 M sulfuric acid solution of the fuel.

The optimum acid concentration of 0.3 M for the separation of iron(III) from uranium(VI) was established by Nelson.[5] He established this by shaking sulfate-form Dowex 1 resin with solutions of radioactive iron-55(III) and uranium-233(VI). These experiments have shown that iron(III) is effectively removed from the resin after the resin is rinsed with one column-volume of 0.3 M sulfuric acid. Additional rinsings are made in order to insure complete separation of the iron from interfering ions. The effluent is collected in a 10-ml volumetric flask that contains 1.47 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ (sodium citrate). When the solution fills the flask to the calibration mark, the iron(III) is in a 0.5 M sodium citrate supporting electrolyte and is ready for polarographic determination.

3.3 Polarography of Iron(III). The polarography of iron(III) in various supporting electrolytes is described by Kolthoff and Lingane.[3] Iron(III) in concentrations less than 10 μg per ml gives a poorly defined wave for the iron(III) iron(II) reduction in a supporting electrolyte of 1 M ammonium oxalate at a half-wave potential of -0.24 volt vs. the S.C.E.[7] A good wave is obtained for the same redox reaction in a supporting electrolyte of 0.5 M sodium citrate at a half-wave potential of -0.15 volt vs. the S.C.E.[4] If the pH of the supporting electrolyte is increased, the half-wave potential becomes more negative and the definition of the wave improves.[4] However, the wave definition is satisfactory at the pH of the 0.5 M sodium citrate solution of the 0.3 M sulfuric acid effluent from the column (~pH 1). It is desirable to eliminate the extra step that would be required if the pH were adjusted.

4. The Ion-Exchange Column

Dowex 1 anion-exchange resin in the sulfate form has a capacity of about 3 milliequivalents of uranium per gram of resin; one gram of resin occupies a volume of about 2 ml. If the volume of resin taken is based on a 1-ml sample of Homogeneous Reactor fuel, which is a practical maximum for highly radioactive fuel, a volume of ~0.1 ml of resin is sufficient. This small volume of resin is impractical

because of channeling and because relatively large volumes of reagents must be added to the sample. A practical resin volume, assuming that the effluent is to be collected in a 10-ml volumetric flask, is 3 ml.

A portion of a 10-ml Mohr pipet makes an excellent ion-exchange column if the lower end is drawn out to a diameter such that the pipet will fit into the neck of a 10-ml volumetric flask. A broken pipet may possibly be used. The pipet provides a clearly graduated space above the resin so that the volume of each increment of water added to the column can be measured accurately. The method of preparing the resin column is described in detail in Section 7.1.1.

5. Results

Table 1 gives the results obtained by the analysis of a synthetic Homogeneous Reactor fuel for iron(III).

6. Acknowledgement

The determination, made by Fred Nelson of the ORNL Chemistry Division, of the optimum conditions for the ion-exchange separation of iron(III) from uranium(VI) contributed greatly to the success of the development of this method.

Table 1. Iron in Synthetic Homogeneous Reactor Fuel

Composition of the fuel:
uranium as uranyl sulfate, 10 mg per ml
copper as cupric sulfate, 2 mg per ml
cobalt as cobaltous sulfate, 0.1 mg per ml
nickel as nickelous sulfate, 0.1 mg per ml
chromium as potassium chromate, 0.1 mg per ml
iron (as indicated), 0.020 to 0.100 mg per ml,
Final dilution for polarographic analysis, 1:10

Iron Present,[a] µg/ml	Iron Found,[a] µg/ml	Rel. Std. Dev., %
10.0	9.8 9.8 9.9 9.9	0.6
5.0	4.8 4.9 4.8 4.9	1.2
2.0	1.95 1.95 1.89 2.18	6.5

(a) Iron in the solution contained in the polarographic cell.

These results indicate that this method is reliable for the determination of iron(III) in Homogeneous Reactor fuels or similar solutions.

7. Appendix

7.1 Method for the Ion-exchange -- Polarographic Determination of Iron(III) in Homogeneous Reactor Fuel

The following procedures were developed as results of the experimental work on this method.

7.1.1 Preparation of the Resin Column

1. Place a plug of glass wool in the tip of the column.

2. Prepare a slurry of chloride-form Dowex 1 anion-exchange resin with distilled water and pour the slurry into the column in increments, allowing the resin to drain after each increment is added, until a volume of 3 ml is filled with resin.

3. Rinse the resin with 1.0 M sodium sulfate solution until the rinsings give a negative test for chloride with silver nitrate solution.

4. Rinse the column with 0.3 M sulfuric acid until the pH of the effluent is the same as that of the influent. Use pH-indicator paper (e.g., Accutint) to determine this.

7.1.2 Removal of Copper from the Fuel

1. From a 1/8-in. wide strip of cadmium sheet metal or from cadmium wire, prepare a coil that will fit inside a 10-ml beaker. Allow enough extra metal for a handle to hang over the edge of the beaker.

2. In order to remove film from the cadmium, insert the coil into a beaker that contains 10 vol % HNO_3, then in distilled water.

3. Place in a 10-ml beaker a sample of Homogeneous Reactor fuel that contains at least 20 μg of iron; insert the clean coil into the beaker.

4. Add enough 0.3 M sulfuric acid to cover the coil, and stir the solution for 15 minutes by means of a magnetic stirrer.

5. Rinse the coil with 0.3 M sulfuric acid, allowing the rinsings to go into the beaker, and add enough potassium permanganate solution to give a pink color.

6. Remove the deposited copper from the cadmium coil by immersing the coil for a few seconds in 10 vol % nitric acid. Rinse the coil with distilled water.

7.1.3 Determination of Iron(III)

1. Place the tip of the resin column into a 10-ml volumetric flask that contains 1.47 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ (sodium citrate).

2. Transfer the contents of the beaker (see Section 7.1.2, Step 5) to the resin column and allow the column to drain.

3. Rinse the beaker with 1 ml of 0.3 M sulfuric acid and transfer the rinsings to the column. Allow the column to drain between rinses.

4. Repeat Step 3 until the volumetric flask is filled to the calibration mark.

5. Shake the solution until all of the sodium citrate is dissolved and pipet an aliquot into a polarographic cell.

6. Obtain a polarogram of the iron(III) $\longrightarrow$ iron(II) reduction at an $E_{1/2}$ of -0.15 volt vs. the S.C.E.

7. Calculate the amount of iron(III) by the standard-addition method.

7.1.4 Removal of Adsorbed Ions from and Regeneration of the Ion-Exchange Resin

1. Rinse the column with 25 ml of 10 vol % sulfuric acid that has been heated to the boiling point. Keep the acid hot between the additions of the increments.

2. Rinse the column with 25 ml of 0.3 M sulfuric acid; it is now ready for re-use.

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