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DETERMINATION OF CORROSION PRODUCTS AND ADDITIVES IN HOMOGENEOUS REACTOR FUEL

II. Polarographic Determination of Chromium

A. D. Horton
P. F. Thomason

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A. D. Horton and P. F. Thomason

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TABLE OF CONTENTS

		PAGE
0.	Abstract	1
1.	Introduction	2
2.	Summary	2
3.	Polarographic Determination of Chromium(III)	4
	3.1 Separation of Chromium(III) from the Fuel	4
	3.2 Polarography of Chromium(III)	5
4.	Polarographic Determination of Chromium(VI)	6
	4.1 Separation of Chromium(VI) from the Fuel	6
	4.2 Determination of Total Chromium	6
	4.3 Polarography of Chromium(VI)	7
5.	Practical Size of the Column of Resin	7
6.	Preparation of the Ion-exchange Column	8
7.	Results	9
8.	Procedures	10
	8.1 Preparation of the Resin Column	10
	8.2 Determination of Chromium(VI)	10
	8.3 Determination of Total Chromium	11
	8.4 Removal of Adsorbed Ions from and Regeneration of the Ion-exchange Resin	11
9.	Bibliography	12

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0. Abstract

A satisfactory ion-exchange—polarographic method was developed for the determination of either chromium(VI) or total chromium in Homogeneous Reactor fuels. Total chromium is determined as chromium(VI), i.e., chromate, and in the same way as is chromium(VI), after chromium in the lower valence states is oxidized to chromate by potassium permanganate. Chromate is separated from all interfering metal ions in the fuel by ion exchange on a Dowex 50 resin column. The chromate in the effluent is determined polarographically in approximately 0.75 M sodium hydroxide solution as supporting electrolyte. A well-defined polarographic wave is obtained for the chromium(VI)$\longrightarrow$chromium(III) reduction at a half-wave potential of -0.85 volt vs. the S.C.E. The relative standard deviation of the data for 2 μg of chromium(VI) per ml was 2%; for 4 μg of total chromium per ml, it was 3%.

An ion-exchange—polarographic method was developed also for the determination of chromium(III). Chromium(III) is separated from all interfering ions in the fuel by ion exchange on a Dowex 1 resin column. The chromium(III) in the effluent is determined polarographically in a 1 M ammonia—1 M ammonium chloride supporting electrolyte. The wave obtained at a half-wave potential of -1.42 volt vs. the S.C.E. is poorly defined, and the method is not entirely satisfactory.

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1. Introduction

At the time of this report, Homogeneous Reactor fuel contains 40 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 the acidity of the fuel. The analytical determination of these contaminant metals is a measure of the corrosion of the components of the reactor system. The determinations of nickel, manganese, copper, and zirconium in Homogeneous Reactor fuel are described by Horton et al. in a previous report.[2]

Chromium(VI) is added to the fuel to inhibit the corrosion of the core and of the attached piping. Most of the chromium(VI) is deposited on the inside metal walls of the system, and only about 10% of that added remains in solution where it is available to be determined. Also, there is evidence that the chromium(VI) that remains in solution is reduced to chromium(III).

2. Summary

A synthetic HR solution was prepared to represent as closely as possible the composition of the fuel as it is at the beginning of normal reactor operation. To the basic fuel that contains uranium, copper, and chromium(VI), were added major corrosion products, such as nickel and cobalt. These corrosion products were added in amounts equal to or greater than the total chromium present. Chromium(III) was added also to represent the most probable valence state of residual chromium during the normal operation of the reactor.

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A typical synthetic fuel composition is as follows: uranium as uranyl sulfate, 40 g per liter; copper as copper sulfate, 2 g per liter; chromium(VI) as potassium dichromate, 0.002 g per liter; chromium(III) as chromic potassium sulfate, 0.002 g per liter; nickel as nickel sulfate, 0.1 g per liter; and cobalt as cobaltous sulfate, 0.1 g per liter.

Chromium(VI) is determined by passing the sample through a Dowex 50 cation-exchange resin column and collecting the effluent in a 10-ml volumetric flask that contains three sodium hydroxide pellets (~300 mg). All the cations in the fuel, including chromium(III), are adsorbed by the resin. The chromium(VI) is rinsed through the column by small increments of water until the volumetric flask is filled to the calibration mark. The resulting solution contains the chromium(VI) in a supporting electrolyte that is approximately 0.75 M sodium hydroxide. The wave for the chromium(VI) $\longrightarrow$ chromium(III) reduction is obtained at a half-wave potential of -0.85 volt vs. the S.C.E.

Total chromium is determined by oxidizing the chromium that is in the lower valence states to chromium(VI) by the addition of a slight excess of potassium permanganate to the sample and boiling the solution before passing it through the column. Both the permanganate and chromate ions pass through the column, but permanganate does not interfere in the polarographic determination of chromate ion.

Chromium(VI), as chromate, in synthetic Homogeneous Reactor fuels has been determined with a relative standard deviation of 2% for a concentration of 2 μg of chromium(VI) per ml and of 3% for 4 μg of total chromium per ml.

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Any amount of chromate ion that is soluble in the fuel will be separated quantitatively from a 1-ml fuel sample on a Dowex 50 resin column that contains three cubic centimeters of resin. For polarographic analysis, the lower limit of determination is 5 μg of total chromium per milliliter of fuel solution.

A method that is inferior to that for chromium(VI) was developed for the determination of chromium(III) in the fuel. Chromium(III) is separated from interfering metals by ion exchange on a Dowex 1 resin column. The effluent that contains the chromium(III) is evaporated to dryness, and the residue is dissolved in 1 ml of 10 M hydrochloric acid and is transferred to a 10-ml volumetric flask. Ammonium hydroxide is added until a 1 M ammonia— 1 M ammonium chloride supporting electrolyte is formed, and the solution is then diluted to volume. A poorly defined polarographic wave is obtained for the chromium(III)$\longrightarrow$chromium(II) reduction at a half-wave potential of - 1.42 volt vs. the S.C.E.

3. Polarographic Determination of Chromium(III)

3.1 Separation of Chromium(III) from the Fuel. Before chromium(III) in Homogeneous Reactor fuel is determined polarographically, all metals that interfere in the determination must be removed from the sample. Dowex 1 ion-exchange resin in the chloride form will not adsorb chromium(III) from hydrochloric acid solutions of any concentration, but will adsorb quantitatively the interfering metal ions in the fuel from a 9 M hydrochloric acid solution of the fuel. One of the problems that is peculiar to the use of high-molarity acid solutions for ion-exchange separations is the large volume of acid rinse that is required to recover quantitatively the desired ion. For a 1-ml sample of Homogeneous Reactor fuel, the column must contain at least 5 cc

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of resin, and a rinse of at least 10 ml of 9 M hydrochloric acid is required. The total effluent must be evaporated to dryness. The residue must then be redissolved in the stoichiometric amount of acid to which a base will be added in order to form the supporting electrolyte. This operation is tedious by remotely controlled analytical techniques, although it is possible and has been done in many cases.

3.2 Polarography of Chromium(III). Polarography of chromium(III) in various supporting electrolytes is described by Kolthoff.[3] Chromium(III) in concentrations of less than 10 μg per ml gives a poorly defined wave for the chromium(III)⟶chromium(II) reduction in a supporting electrolyte of 1 M ammonia— 1 M ammonium chloride at a half-wave potential of -1.42 volts vs. the S.C.E.[9] Pronounced maxima were obtained in this medium, and they were not entirely suppressed by the addition of gelatin or by a decrease in the concentration of the electrolyte. A better wave is obtained for the same redox reaction in a supporting electrolyte of 0.1 M pyridine — 0.1 M pyridinium chloride at a half-wave potential of -0.95 volt vs. the S.C.E.[5] However, the nickel(II)⟶nickel reduction occurs at a half-wave potential of -0.78 volt vs. the S.C.E.,[4] and the separation of the waves is not good. Also, the nickel concentration of the Homogeneous Reactor fuel may possible be as much as ten times that of the chromium(III) concentration, in which case the chromium wave will be masked completely by the nickel wave. The concentrations of the supporting electrolytes in these cases are not critical, and the supporting electrolytes can be made by adding a suitable base to the redissolved acidic residue mentioned above. Suitable pH indicators can be used to show approximately

when sufficient base has been added to form the supporting electrolyte. The necessity for redissolving the residue in acid precludes the use of neutral supporting electrolytes, such as those used in the methods of Prajzler,[8] of Demassieux and Heyrovsky,[1] and of Lingane and Pecsok,[7] because of the difficulty of exactly neutralizing acidic solutions of the residue.

4. Polarographic Determination of Chromium(VI)

4.1 Separation of Chromium(VI) from the Fuel. A cation-exchange resin is ideally suited to the separation of chromate ion from metals in Homogeneous Reactor fuel. When the fuel that contains chromate ions is passed through Dowex 50 cation-exchange resin, all the cations present, which include all metal ions that interfere in the polarographic determination of chromate ion, are adsorbed, and the chromate passes through quantitatively.

The fuel is introduced onto the column without pretreatment, and the effluent is collected in a 10-ml volumetric flask that contains three pellets ($\sim$300 mg) of sodium hydroxide. When the solution fills the flask to the calibration mark, the chromate ion is in an approximately 0.75 M sodium hydroxide supporting electrolyte and is ready for polarographic determination.

4.2 Determination of Total Chromium. Chromium that is in lower valence states must be oxidized to chromate ion before the sample is introduced onto the column. Potassium permanganate is the simplest and most rapid oxidant for this purpose. A slight excess of the permanganate is added to the sample, and the solution is heated to boiling. After the solution is cooled, it is introduced onto the Dowex 50 resin column, and the procedure for the polarographic determination of chromium(VI) (see Section 4.3) is followed. Permanganate ion,

fission-product metal anions, such as ruthenate, and metal anions formed by chemical oxidation of the fuel do not interfere in the polarographic determination of chromate ion.

4.3 Polarography of Chromium(VI). The chromium(VI)$\longrightarrow$chromium(III) reduction gives a well-defined wave for chromium(VI) concentrations as small as 0.5 μg per ml at a half-wave potential of -0.85 volt vs. the S.C.E. in a supporting electrolyte of 1 M sodium hydroxide.[6] This concentration of sodium hydroxide tends to produce maxima, but a maxima-free wave is obtained when 0.75 M sodium hydroxide solution is used. The polarographic reduction of chromium(VI) has an advantage over that of chromium(III) because there is a three-electron change in the chromium(VI)$\longrightarrow$chromium(III) reduction as compared with a one-electron change in the chromium(III)$\longrightarrow$chromium(II) reduction. Thus the diffusion current for the reduction of chromate to chromium(III) is three times as great as that for the reduction of chromium(III) to chromium(II).

5. Practical Size of the Column of Resin

Dowex 50 cation-exchange resin has a capacity of about 4 milliequivalents per gram of resin, and this quantity of resin occupies a volume of about 2 ml. If the resin volume taken is based on a sample size of 1 ml, which is a practical maximum for highly radioactive fuel, a volume of 0.75 ml of resin is sufficient. This small volume of resin is impractical because of channeling, and of relatively large volumes of reagents 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 1-ml volume of sample plus a minimum of two column volumes used to remove the chromate from the column totals 7 ml. Passage of an additional 3 ml of water through the column gives a safety factor that insures quantitative removal of the chromate ion.

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6. Preparation of the Ion-exchange Column

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 accurately measured. See Section 8.1 for the method of preparation of the resin column.

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7. Results

Table 1 gives the results obtained by the analysis of synthetic Homogeneous Reactor fuels for chromium(VI) and total chromium.

Table 1. Chromium in Synthetic Homogeneous Reactor Fuels

Composition of the fuels:

uranium as uranyl sulfate, 40 mg per ml
copper as copper sulfate, 2 mg per ml
cobalt as cobaltous sulfate, 0.1 mg per ml
nickel as nickelous sulfate, 0.1 mg per ml
chromium in sample A as chromium(III), 0.020 mg per ml
in sample B as chromium(III), 0.020 mg per ml
as chromium(VI), 0.020 mg per ml

Final dilution for polarographic analysis, 1:10

Sample	Cr(VI) Found, µg/ml	Rel. Std. Dev., %	Total Cr found, µg/ml	Rel. Std. Dev., %
A	---	---	1.94	2.8
			2.02	
			1.96	
			2.08	
			1.99	
B	1.94	2.2	3.98	3.1
	1.92		3.80	
	1.99		3.99	
	1.98		4.10	
	2.03		4.10	

These results indicate that the method described is reliable for the determination of chromium in Homogeneous Reactor fuels or similar solutions.

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8. Procedures

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

8.1 Preparation of the Resin Column

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

2. Prepare a slurry of Dowex 50 cation-exchange resin with water, and pour it into the column in increments, allowing the resin to drain after each increment is added, until the 3-ml volume is filled with resin.

3. Rinse the resin with 100 ml of 6 M sulfuric acid, then with an equal volume of water before adding a sample.

8.2 Determination of Chromium(VI)

1. Place the bottom tip of the Dowex 50 cation-exchange column into the neck of a 10-ml volumetric flask that contains three pellets of NaOH (~ 300 mg).

2. Pipet a volume of Homogeneous Reactor fuel that is estimated to contain at least 5 μg of chromium(VI) onto the column.

3. Allow the sample to pass through the column by gravity flow.

4. When the column has nearly drained, add water in approximately 2-ml increments until the flask is filled to just below the calibration mark.

5. Fill the flask to the calibration mark, mix the contents completely, and pipet an aliquot of the solution into the polarographic cell.

6. Obtain a polarographic wave of the chromium(VI)$\longrightarrow$chromium(III) reduction at an $E_{1/2}$ of -0.85 volt vs. the S.C.E.

7. Calculate the amount of chromium(VI) by the standard-addition method.

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8.3 Determination of Total Chromium

1. Into a 10-ml beaker, pipet a volume of Homogeneous Reactor fuel that is estimated to contain at least 5 μg of total chromium.

2. Add a slight excess of potassium permanganate solution (enough to give the sample solution a deep pink color).

3. Heat the solution to boiling, then cool it.

4. Position the tip of the column into the neck of a 10-ml volumetric flask that contains three pellets of NaOH (~300 mg).

5. Pour the contents of the beaker onto the column and rinse the beaker well with 2-ml increments of water. Allow the column to drain almost completely dry between the addition of increments of water.

6. Continue as before with Steps 5, 6, and 7 of part 8.2 above.

8.4 Removal of Adsorbed Ions from and Regeneration of the Ion-exchange Resin

1. Pass about 25 ml of 6 M H_2SO_4 through the resin to remove adsorbed ions.

2. Pass about 25 ml of distilled water through the resin to regenerate the resin before the next sample is added.

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