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DETERMINATION OF CORROSION PRODUCTS AND ADDITIVES IN HOMOGENEOUS REACTOR FUEL

A. D. Horton
P. F. Thomason
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DETERMINATION OF CORROSION PRODUCTS AND ADDITIVES IN HOMOGENEOUS REACTOR FUEL

A D Horton, P F Thomason, and M T Kelley

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0 0 ABSTRACT

Nickel and manganese have been separated from uranium in 6 M hydrochloric acid solutions of Homogeneous Reactor fuel by ion exchange on a Dowex A-1 chloride-form resin column and determined simultaneously by polarography in ammonia-ammonium chloride electrolyte The relative standard deviation of this method is 3 7% for nickel at a concentration of 10 µg per ml and 6 5% for manganese at a concentration of 2 0 µg per ml

Nickel and manganese have been separated from uranium in 0 005 M sulfuric acid solutions of HR fuel by ion exchange on a Dowex A-1 sulfate-form resin column and determined simultaneously by polarography in ammonia-ammonium sulfate electrolyte The relative standard deviation of this method is 5% for nickel at a concentration of 2 0 µg per ml and 3 4% for manganese at a concentration of 2 0 µg per ml

The lower limit of sensitivity of the methods is 0 5 µg of nickel or manganese per ml of the solution used for the polarographic analysis

Copper in HR fuel has been determined by polarography of a 0 25 M disodium dihydrogen ethylenediaminetetraacetate solution of the fuel at pH 8 5 The half-wave potential of copper in this medium is approximately - 0 55 volt vs the S C E By this method, copper in HR fuel has been determined in concentrations of 1 to 10 µg per ml The relative standard deviation of the method is 0 65% for copper at a concentration of 10 µg per ml

Zirconium has been separated from uranium in 6 M hydrochloric acid solutions of HR fuel by ion exchange on a Dowex A-1 chloride-form resin column

[redacted]

and determined spectrophotometrically as the 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid (Thoron) complex at a wavelength of 555 mμ The range of the method is 10 to 100 μg of Zr, and the relative standard deviation is 4 2% for this range

[redacted]

1 0 INTRODUCTION

The study of corrosion is an integral part of the Homogeneous Reactor Project The acidic fuel in contact with the metallic core and attached piping of the reactor inevitably dissolves some of the metal Analysis of the fuel for certain metals provides an indication of the amount of corrosion

Where stainless steel is used as the reactor core, corrosion is indicated by the presence of nickel, and to a lesser extent manganese, in the reactor fuel Likewise, if zirconium or its alloys are used in the reactor, the presence of zirconium in the fuel indicates the extent of corrosion

Copper is added to the HR fuel to catalyze the recombination of hydrogen and oxygen that are produced in large quantities by the action of radiation on water in the fuel during the operation of the reactor It is necessary to determine copper in order to study its effect on the overall operation of the reactor

2 0 SUMMARY

Nickel and manganese are separated from uranium in 6 M hydrochloric acid or 0 005 M sulfuric acid solutions of HR fuel by means of Dowex A-1 chloride - or sulfate-form ion-exchange resin The effluent that contains the nickel and manganese is collected in a polarographic cell and is evaporated to a volume of 0 2 to 0 5 ml for chloride solutions or approximately 4 ml for sulfate solutions In either case, the sample is diluted to 4 ml with distilled water and one drop of 0 2% solution of phenolphthalein in ethanol is added

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Sufficient ammonium hydroxide is added to obtain a permanent pink color and the sample is then diluted to the cell calibration mark Polarograms are obtained for nickel at $E_{1/2}$ = -1 05 volt vs the S C E and for manganese at $E_{1/2}$ = -1 45 volt vs the S C E The relative standard deviation obtained by use of chloride-form resin is 3 7% for 10 µg of nickel and 6 5% for 2 µg of manganese, and when sulfate-form resin is used, 5 0% for 2 µg of nickel and 3 4% for 2 µg of manganese The minimum amounts of nickel and manganese in the sample must be 2 5 µg of each The only interference in HR fuel at the present time is uranium The method is recommended for the determination of nickel and manganese in HR fuel because the amount of manipulation required is less than that required in other methods of the same range of sensitivity as this method

Zirconium is separated from uranium by passing a 5 M hydrochloric acid solution of the sample through a chloride-form, Dowex A-1 ion-exchange resin Uranium remains on the column and zirconium passes through quantitatively The effluent is evaporated to dryness, the residue is dissolved in 0 25 ml of concentrated hydrochloric acid, and the zirconium in the sample is determined spectrophotometrically as the 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid (Thoron) complex at a wavelength of 555 mµ versus a reference of reagents The range of the method is 10 to 100 µg of zirconium per sample The volume range is limited only by such factors as radioactivity, vessel size, and time The resin capacity is approximately 4 milliequivalents of uranium per gram of resin, suitable column size can be determined by consideration of the resin capacity plus the factors

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mentioned above The relative standard deviation of the method in the range 10 to 100 μg of zirconium per 10-ml volume is 4 2%

Pecsok's method for the polarographic determination of copper in 0 25 M disodium dihydrogen ethylenediaminetetraacetate (Versenate) solution has been modified and used to determine copper in HR fuel solutions One volume of HR fuel solution is adjusted to a pH of approximately 3 with solid sodium carbonate and diluted with an equal volume of 0 5 M Versenate solution that has been adjusted to pH 7 0 with solid sodium carbonate, then to pH 8 5 with concentrated sodium hydroxide solution A convenient aliquot of the Versenate solution of the sample is pipeted into the polarographic cell and copper is determined at $E_{1/2}$ = -0 55 volt vs the S C E The D M E is used as the indicating electrode The sequestering action of the Versenate solution at pH 8 5 gives a more negative value to the half-wave potential of copper than its half-wave potential in acid solution Other metals in HR fuel solutions do not interfere Test volumes of the sample are limited only by practicality, and the quantity range of the method is limited only by the sensitivity of the polarograph used for the determination The relative standard deviation of the method is 0 65% for a copper concentration of 10 μg per milliliter

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3 0 SIMULTANEOUS POLAROGRAPHIC DETERMINATION OF NICKEL AND MANGANESE

3 1 Separation of Uranium by Ion-Exchange

Investigations of the corrosion of stainless steels that had been immersed in uranyl sulfate solutions for known periods of time showed that the amounts of dissolved nickel, and to a lesser extent manganese, provide an accurate indication of the corrosion rate of the steel

In the determination of nickel and manganese in HR fuel, consideration must first be given to the separation of uranium from these metals Uranium interferes in the polarographic determination of nickel and manganese because it is present in the fuel in 40 to 400 times the amounts of nickel and manganese Also, uranium precipitates in ammonia-ammonium chloride solution, which is the supporting electrolyte for nickel and manganese, and tends to coprecipitate part of the nickel According to Moore and Kraus[9], uranium can be separated from nickel and manganese by use of Dowex A-1 chloride- or sulfate-form ion-exchange resin The resin column dimensions will vary according to the capacity of the resin for adsorption of uranium and to the concentration of uranium in the sample Dowex A-1 chloride-form resin has a capacity of approximately one milliequivalent of uranium per gram of resin The capacity of the sulfate-form resin is slightly higher Homogeneous reactor fuel contains 40 mg of uranium per ml or 0 34 milliequivalents per milliliter If the samples are taken at full strength, the estimated capacity of a 5-ml column-volume (actual volume of resin body within the glass column) (Fig 1) would be 300 mg of uranium or 7 5 ml of sample, since the weight of resin is approximately 0 5 g per milliliter Reactor samples are usually diluted 100 1 (v/v), therefore a column of this size can be used many times

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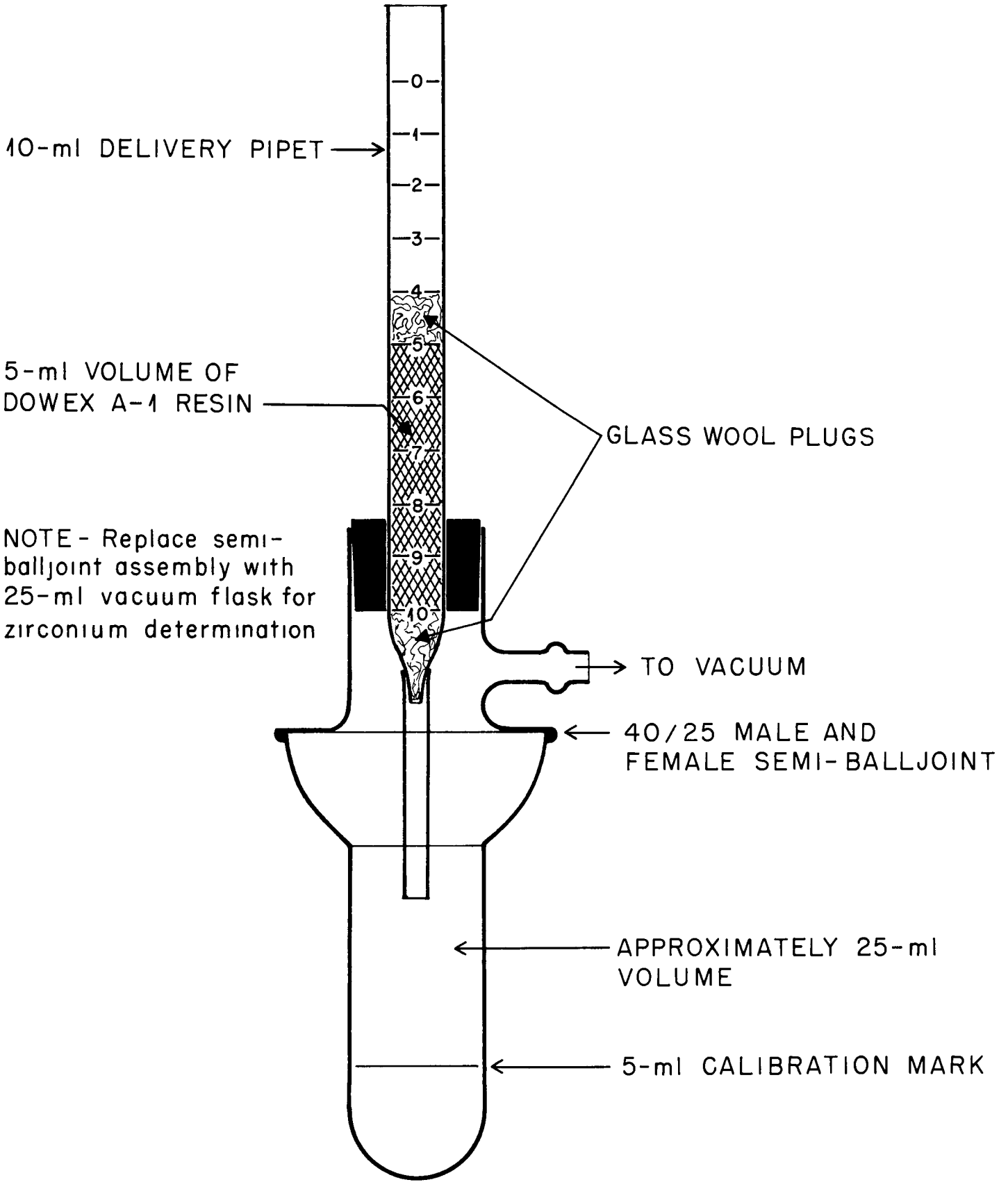

FIG 1 DOWEX A-1 ION EXCHANGE RESIN COLUMN FOR SEPARATING URANIUM FROM CORROSION PRODUCTS IN HOMOGENEOUS REACTOR FUEL

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before it needs to be reactivated

The recommended rate of flow of samples through the column is 0 5 ml per cm^2 cross-sectional area of the resin per minute Thus the flow rate of sample through a column of 1-cm diameter would be 0 5 ml per minute The amount of rinse required for the quantitative recovery of the nickel and manganese from the column is two column-volumes The acidic rinse solution must be the same acid and acid molarity as that of the sample solution, and it should be added in four or more equal increments After the addition of each increment, the solution level should be allowed to fall to 0 5 inch above the resin level

If the chloride-form resin is used, the hydrochloric acid concentration of the sample before it is introduced onto the column should be 6 M which is optimum The volume of effluent, which is large with respect to the amount of nickel and manganese, must be evaporated almost to dryness in order to increase the HCl concentration to the amount required for the formation of the ammonia-ammonium chloride supporting electrolyte Adjustment of the pH of the hydrochloric acid solution of the metals to the phenolphthalein end point with ammonium hydroxide and dilution to the desired volume produce a solution that is ready for polarographic analysis

Sulfate-form resin can be used with results comparable with those for chloride-form resin The optimum concentration of sulfuric acid in the sample solution is 0 005 M The HR fuel sample is received in sulfate medium, and very little sulfuric acid need be added to adjust the acid concentration to 0 005 M Therefore, smaller volumes of sample are

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required with the sulfate-form than with the chloride-form resin The column must be rinsed with at least two column-volumes of 0 005 M sulfuric acid, but the evaporation of the effluent to a volume of about 1 ml below the calibration mark of the cell (Fig 1) is sufficient to allow pH adjustment to the phenolphthalein end point with ammonium hydroxide

3 2 Polarography of Nickel and Manganese

Nickel gives a well-defined wave in ammonia-ammonium chloride or ammonia-ammonium sulfate supporting electrolyte at $E_{1/2} = -1$ 05 volt vs the S C E ,[7] by use of the D M E as the indicating electrode Manganese gives a fairly well-defined wave at $E_{1/2} = -1$ 45 volt vs the S C E [1] The final concentration of supporting electrolyte is not critical. When the chloride-form resin is used according to procedure, the concentration of the supporting electrolyte will vary from approximately 0 2 to 0 5 M If sulfate-form resin is used, the concentration of the supporting electrolyte will be 0 005 to 0 01 M In either case, the concentration of supporting electrolyte is satisfactory for concentrations of 0 5 to 10 µg of nickel or manganese per ml The standard addition technique[3] is used to determine the concentrations of nickel and manganese in the sample

3 3 Recommended Procedures

All reagents used in this work were analytical-reagent grade chemicals The modified Sargent model 20 polarograph was used for all the polarographic studies

A Purification of the Resin and Preparation of the Resin Column

1 To obtain chloride-form resin, purify Dowex A-1 ion-exchange resin by the method of Foster[2]

[redacted]

2 To convert chloride-form resin to sulfate-form, pass through it 20 column-volumes of 0 5 M sulfuric acid, then 20 column-volumes of 0 005 M sulfuric acid

3 Prepare the column for use by mixing the purified resin of the proper form with 6 M hydrochloric acid or 0 005 M sulfuric acid to form a slurry that can be easily poured into the column

4 Place a plug of glass wool in the bottom of the column and fill the column with slurry to the 5-ml level (see Fig 1)

5 Place a plug of glass wool on top of the column to prevent disturbance of the resin body

6 Maintain the solution level at least 0 5 inch above the resin level at all times to prevent channeling in the column

B Determination of Nickel and Manganese by Use of Chloride-Form Resin

1 Attach the female section of the semi-balljoint of the polarographic cell to the bottom of the column (see Fig 1)

2 To the desired volume of sample, add an equal volume of concentrated hydrochloric acid (~12 M)

3 Introduce the sample onto the column and allow it to pass through the column until the solution level is about one-half inch above the resin level Use vacuum, if necessary

4 Add at least two column-volumes of 6 M hydrochloric acid in 2-ml increments, allowing the solution level to fall to 0 5 inch above the resin after each addition

5 Remove the female section of the semi-balljoint and place it under an infrared lamp

[redacted]

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6 Evaporate the solution to 0 2 to 0 5 ml (estimated), then add one drop of a 0 2% solution of phenolphthalein in ethanol

7 Add sufficient ammonium hydroxide to obtain a permanent pink color Do not add an excess Dilute the sample to the calibration mark of the polarographic cell (see Fig 1)

8 Transfer the female section of the semi-balljoint to the polarographic cell and deoxygenate the solution with purified nitrogen for 10 minutes

9 Determine nickel at an $E_{1/2}$ = -1 05 volt vs the S C E and manganese at an $E_{1/2}$ = -1 45 volt vs the S C E Use the standard addition technique[3] to determine the amount of nickel and manganese in the sample

C Determination of Nickel and Manganese by Use of Sulfate-Form Resin

1 Follow Step 1 of Part B above

2 To the desired volume of sample, add sufficient 3 M sulfuric acid to make a 0 005 M sulfuric acid solution of the sample

3 Follow Steps 3 through 5 of Part B, substituting 0 005 M sulfuric acid for 6 M hydrochloric acid

4 Evaporate the solution to approximately 0 5 ml below the calibration mark, allow the solution to cool, then add one drop of 0 2% solution of phenolphthalein in ethanol

5 Follow Steps 7 through 9 of Part B

D Removal of Uranium From the Ion Exchange Column

To remove uranium from the chloride-form resin, rinse the column with 0 1 M hydrochloric acid To remove uranium from the sulfate-form resin, rinse the column with 3 M sulfuric acid

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3 4 Results and Discussion

The characteristics of the polarographic waves of nickel and manganese are illustrated in Fig 2 The results obtained from the polarographic determination of nickel and manganese in synthetic HR fuel are shown in Table 1 Metallic contaminants, other than uranium, do not interfere in

Table 1

Nickel and Manganese in Synthetic HR Fuel Solution

Nickel (Nickel Taken, 10 μg per ml)			Manganese (Manganese Taken, 2 μg per ml)		
Nickel Found, μg/ml	Difference μg/ml	Difference %	Manganese Found, μg/ml	Difference μg/ml	Difference %
		A Chloride-form Resin			
10 02	+0 02	+0 2	1 90	-0 10	-5 0
10 10	+0 10	+1 0	2 00	0 00	0 0
9 80	-0 20	-2 0	1 80	-0 20	-10 0
10 90	+0 90	+9 0	1 95	-0 05	-2 5
9 50	-0 50	-5 0	1 95	-0 05	-2 5
10 31	+0 31	+3 1	1 99	-0 01	-0 5
9 88	-0 12	-1 2	1 97	-0 03	-1 5
9 88	-0 12	-1 2	2 05	+0 05	+2 5
10 06	+0 06	+0 6	2 04	+0 04	+2 0
9 82	-0 18	-1 8	2 12	+0 12	+6 0
10 24	+0 24	+2 4	2 09	+0 09	+4 5
10 02	+0 02	+0 2	2 16	+0 16	+8 0
10 70	+0 70	+7 0	1 93	-0 07	-3 5
9 30	-0 70	-7 0			
		B Sulfate-form Resin			
2 11	+0 11	+5 5	2 02	+0 02	+1 0
2 11	+0 11	+5 5	1 93	-0 07	-3 5
1 91	-0 09	-4 5	1 87	-0 13	-6 5
2 04	+0 04	-2 0	1 83	-0 17	-8 5
1 87	-0 13	-6 5			

the determination of nickel and manganese by this method A copper wave has been noted at an $E_{1/2}$ = -0 24 volt vs the S C E , but the wave is not

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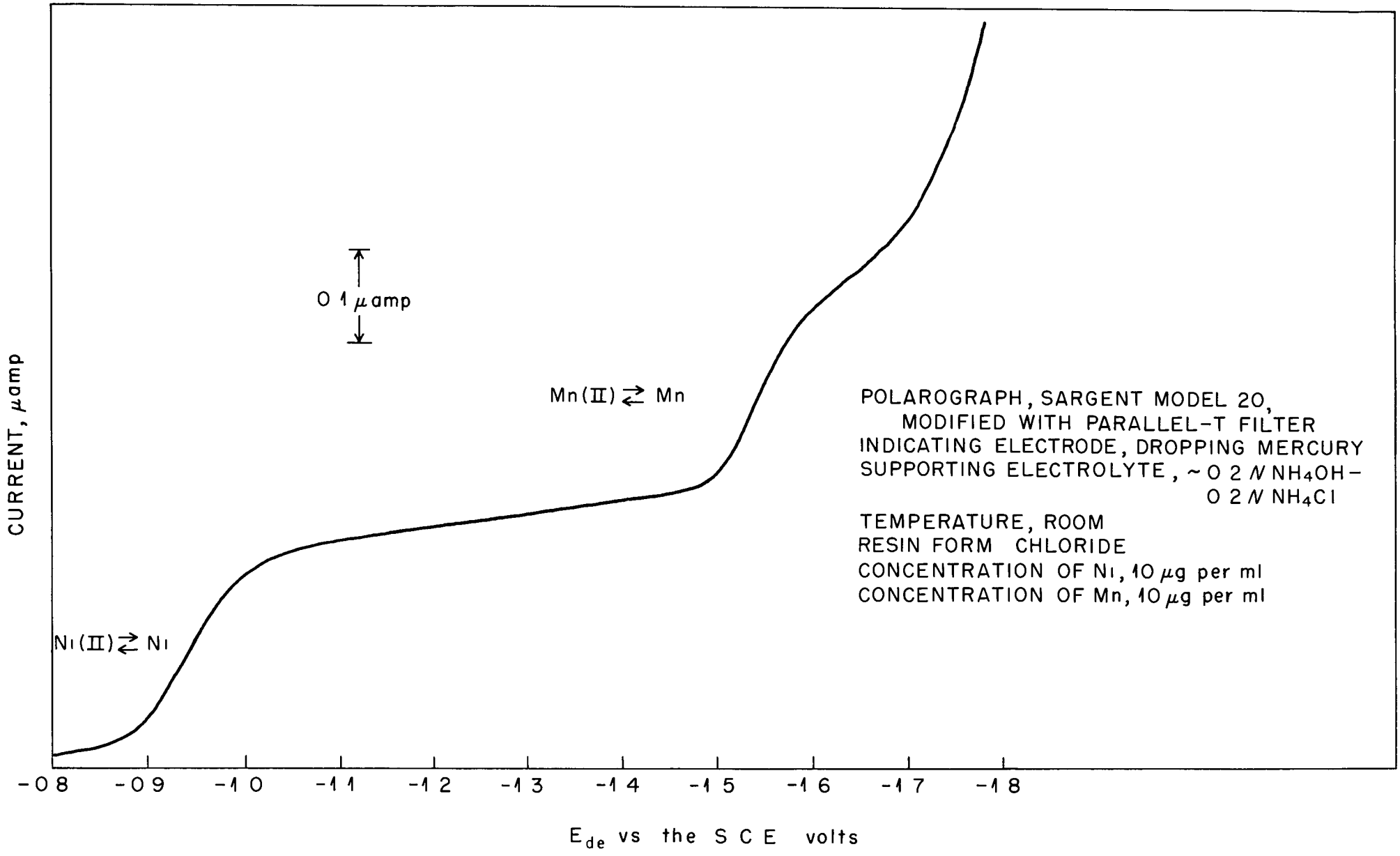

FIG 2 - POLAROGRAMS OF NICKEL AND MANGANESE IN SYNTHETIC HR FUEL SOLUTION TAKEN SIMULTANEOUSLY AFTER REMOVAL OF URANIUM ON DOWEX A-1 ION-EXCHANGE RESIN

well-defined in the supporting electrolyte used in this procedure

The procedure that utilizes the sulfate-form resin has two advantages over that which uses the chloride-form resin First, the volume of sample required is much smaller (an important consideration for radioactive solutions), and second, much less evaporation time is required for the effluent These advantages result, primarily, in a saving of time Otherwise, there is no choice between the two resins, the results obtained indicate approximately the same precision for both procedures The relative standard deviation when chloride-form resin is used is 3 7% for nickel and 6 5% for manganese When sulfate-form resin is used, the relative standard deviation is 5% for nickel and 3 4% for manganese These values were calculated from data in Table 1

4 0 POLAROGRAPHIC DETERMINATION OF COPPER

The effect of copper additives in HR fuel upon the operation of the reactor is determined in part by analyzing the fuel for copper

4 1 Polarography of Copper in Supporting Electrolyte of Disodium Dihydrogen Ethylenediaminetetraacetate

Pecsok[10] reported that copper gave a well-defined polarographic wave in a 0 25 M solution of the disodium dihydrogen salt of ethylenediaminetetraacetic acid, hereinafter called Versenate solution, that had been adjusted to pH 6 to 9 with sodium carbonate It was reported that the half-wave potential varied from -0 22 to -0 46 volt vs the S C E by use of the D M E, depending on the pH of the Versenate solution The higher the pH, the more negative was the half-wave potential The complexing action of the Versenate on the copper shifts the half-wave potential of copper to a value at least

[redacted]

0 4 volt more negative than the value in nitric acid solution The half-wave potential of copper in this medium is -0 01 volt vs the S C E ,[11] when the D M E is used as an indicator electrode Because of the preferential sequestering action of the Versenate on the copper in HR fuel at pH 8 5, only copper gives a polarographic wave

To test the value of Versenate in the determination of copper in the presence of a relatively large amount of uranium, a synthetic HR fuel solution was made to contain 40,000 ppm of uranium (added as UO_2SO_4), 1000 ppm of nickel (as $NiSO_4$) and 100 ppm of iron (as $Fe_2(SO_4)_3$) One milliliter of this solution was diluted to 100 ml with distilled water to correspond to the dilution usually made to HR fuel samples Prior to dilution, sufficient copper sulfate was added to give a final concentration of 2 ppm of copper Versenate solution (0 5 M) was prepared by adding 18 6 g of disodium dihydrogen ethylenediaminetetraacetate to double-distilled water and adjusting the pH to 6 0 with solid sodium carbonate The solution was diluted to 100 ml with double-distilled water To 5 ml of the diluted synthetic fuel was added 5 ml of the 0 5 M Versenate solution A polarogram of this solution produced a copper wave at $E_{1/2}$ = -0 5 volt vs the S C E However, there was no limiting current (see Fig 3) The half-wave potential of the copper wave at pH 6.0 apparently coincided with the residual current of one of the other metals in the sample The pH was adjusted gradually upward with sodium hydroxide solution, a new polarogram being run after the addition of each increment of sodium hydroxide solution When a well-defined wave

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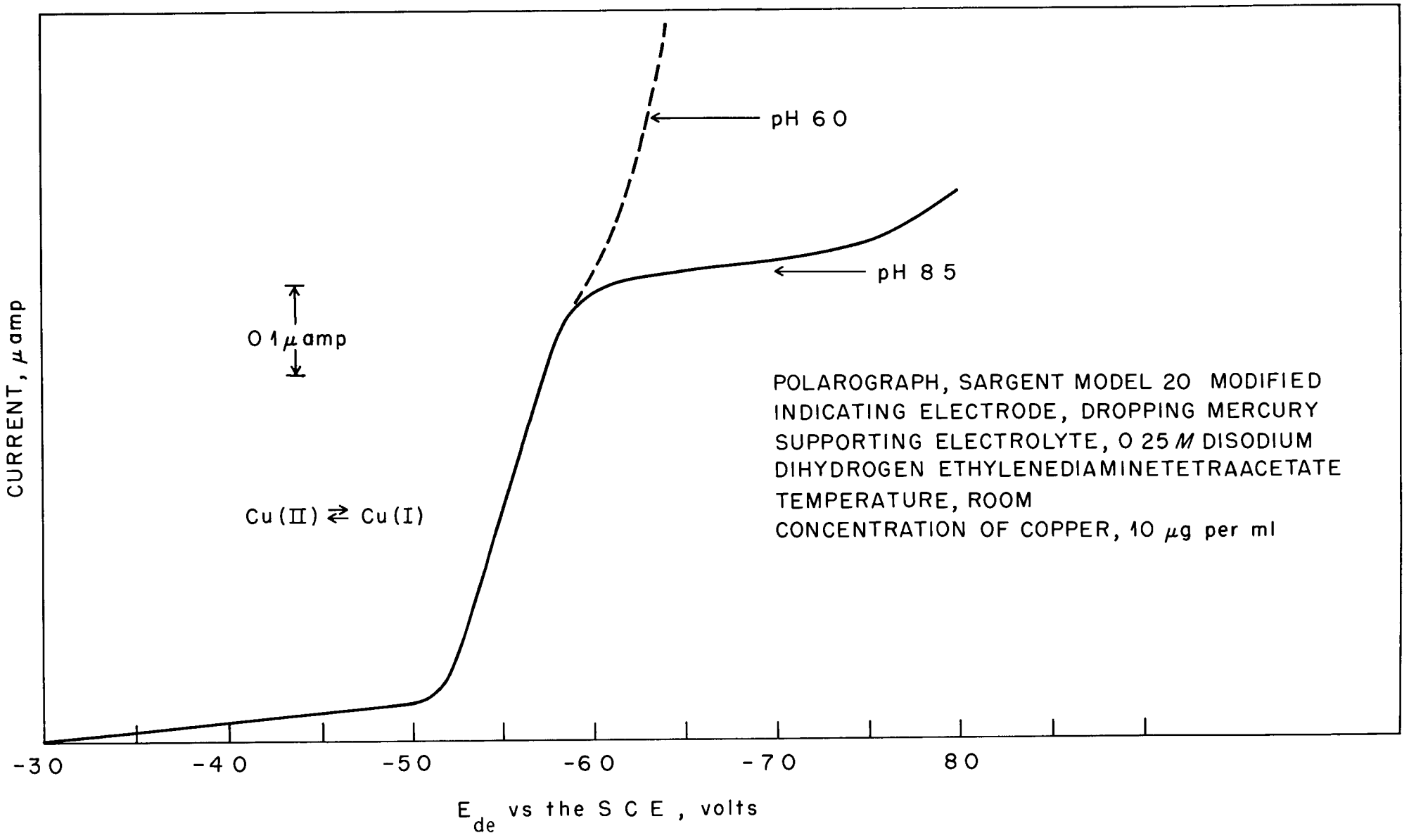

Fig 3 - EFFECT OF pH ON THE LIMITING CURRENT OF THE POLAROGRAPHIC WAVE FOR THE COPPER-VERSENATE COMPLEX

[redacted]

was obtained, the pH of the solution was checked and found to be 8 5 The half-wave potential of copper at this pH was -0 55 volt vs the S C E The increase in the pH of the Versenate solution caused a negative shift in the half-wave potential of copper of only 0 05 volt, but the sequestering action of Versenate for copper is greater at pH 8 5 than that for the other metals in the sample

4 2 Recommended Procedures

From the information obtained in these experiments, the following procedure was developed for the polarographic determination of copper in HR fuel solution

A Preparation of 0 5 M Versenate Supporting Electrolyte

1. Weigh 18 60 g of reagent-grade disodium dihydrogen ethylenediaminetetraacetate into a 150 ml beaker
2. Add enough double-distilled water to facilitate stirring, and lower pH electrodes into the solution
3. Add solid, reagent-grade sodium carbonate until the pH is 7 0
4. Add solid sodium hydroxide until the pH approaches 8 5, then make the final adjustment to pH 8 5 with a solution of sodium hydroxide in double-distilled water

[redacted]

[redacted]

5 Transfer the solution to a 100-ml volumetric flask and dilute it to 100 ml with double-distilled water

B Preparation and Polarography of the Sample

1 If the pH of the sample is less than 3, adjust the pH to approximately 3 with solid sodium carbonate

2 Pipet the desired volume of the sample into the polarographic cell and add an equal volume of 0 5 M Versenate solution

3 Deoxygenate the solution for 10 minutes with purified nitrogen

4 Obtain the polarogram for copper at an $E_{1/2} = -0\ 55$ volt vs the S C E by use of the D M E

5 Determine the concentration of the copper in the sample by the standard addition technique[3]

4 3 Results and Discussion

Copper in the radioactive HR fuel can be determined readily by this method because the amount of manipulation of the sample is very small A large number of samples can be analyzed in one shift because of the simplicity of the method Results obtained from polarograms of synthetic HR fuel solutions that contained copper are shown in Table 2

[redacted]

[redacted]

Table 2

Polarographic Determination of Copper in Synthetic HR Fuel Solutions

Copper Taken, µg/ml	Copper Found, µg/ml	Deviation µg/ml	Deviation %
1 0	0 98	-0 02	-2 0
	1 02	+0 02	+2 0
4 0	3.97	-0.03	-0 8
	4.04	+0 04	+1 0
6 0	5 99	-0 01	-0 2
	6 01	+0 01	+0 2
10 0	10 1	+0 10	+1 0
	10 0	--	--

The relative standard deviation of this method is 0 65% (5)

5 0 SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

In a reactor that contains zirconium metal or its alloys, the uranium solution that is used in the reactor will contain the zirconium as a contaminant The analytical determination of zirconium is a requisite to the study of corrosion of the zirconium-containing components of the reactor

5 1 Spectrochemical Properties of Thoron and Zirconium-Thoron Complex

Zirconium has been determined spectrophotometrically(4) as the 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid (Thoron) complex Solutions that contain zirconium in the concentration range of 10 to 100 µg of zirconium per 10 ml of final volume are made acidic with concentrated hydrochloric acid, and Thoron reagent is added to form the blood red

[redacted]

[redacted]

zirconium-Thoron complex The samples are heated at 75° C for 5 minutes and absorbancies of the solutions are determined spectrophotometrically at a wavelength of 555 mμ versus a reference solution that contains all reagents Uranium is the only component of HR fuel that will interfere in the method Large concentrations of uranium in the samples will form a complex with Thoron that has a small but significant absorbancy at 555 mμ

5 2 Separation of Uranium by Ion-Exchange

According to Kraus et al [8], uranium can be separated from zirconium by Dowex A-1 ion-exchange resin in 5 M hydrochloric acid solution Uranium remains in the resin column and zirconium passes through The hydrochloric acid solution of zirconium must be evaporated to dryness, the residue dissolved, and the solution made 0 4 M in hydrochloric acid before the chromogenic reagent is added

5 3 Recommended Procedures

Reagents and Apparatus Analytical-reagent grade chemicals were used in all experiments The Beckman model DU quartz spectrophotometer with cells of 1-cm light-path length was used for all absorbancy readings

A Preparation of the Dowex A-1 Ion-Exchange Resin Column

Prepare the resin according to the method given for chloride-form resin, Section 3 3, Part A, but use 5 M instead of 6 M hydrochloric acid

B Preparation of the Sample and Determination of Zirconium

1 To the desired volume of sample, add an equal volume of 10 M hydrochloric acid

2 Pipet the sample onto the prepared column

[redacted]

[redacted]

3 When the solution level has fallen to about one-half inch above the resin level, pipet at least two column-volumes of 5 M hydrochloric acid onto the column in 2-ml increments

4 After the addition of all the rinse solution, allow the solution level to fall to one-half inch above the resin level

5 Evaporate the solution to dryness

6 Add 7 drops of concentrated hydrochloric acid and rinse the sample into a 10-ml volumetric flask

7 Add 5 drops of 20% hydroxylamine hydrochloride solution and 1 ml of 0 2% Thoron reagent

8 Dilute the sample to volume

9 Prepare a reference by diluting 1 ml of 0 2% Thoron reagent and 7 drops of concentrated hydrochloric acid to 10 ml in a 10-ml volumetric flask

10 Heat the sample and reference solutions to 75° C in a water bath, and maintain the temperature between 75 and 80° C for 5 minutes

11 Cool the solution to room temperature and use the reference to set the spectrophotometer at 0 0 absorbancy

12 Determine the absorbancy of the sample versus the reference at 555 mμ

13 Determine the concentration of zirconium from a calibration curve prepared by treating standard zirconium solutions (range of 10 to 100 μg of zirconium per 10-ml volume) by this procedure

[redacted]

[redacted]

5 4 Results and Discussion

In Part B, Step 5 of Section 5 3, the solution should be evaporated just to dryness, but not allowed to bake on the glass This requires close attention to the sample, the point at which the sample should be removed from the heat can be determined by noting when the solution in the bottom of the beaker stops bubbling A small amount of residual acid will not significantly vitiate the results and is preferable to baking the residue, which makes removal of the residue from the glass almost impossible, thereby causing low results

Another source of error is the passing through the column of very fine particles of resin, which will adsorb Thoron reagent from the test solution and cause low results This can be prevented by using a glass-wool plug of sufficient bulk in the bottom of the column and by washing the column with large quantities of 5 M hydrochloric acid before it is used in order to assure the removal of the very fine particles of resin A further precaution of filtering the effluent through No 42 filter paper before evaporation can be taken if necessary

The results obtained by separating zirconium from uranium and determining the zirconium spectrophotometrically are shown in Table 3

[redacted]

[redacted]

Table 3

Spectrophotometric Determination of Zirconium in Synthetic HR Fuel Solutions

Unknown Sample No	Zirconium Present, µg/ml	Zirconium Found, µg/ml	Deviation µg/ml	Deviation %
A	62 0	59 3	-2 7	4 4
B	30 0	29 5	-0 5	1 7
C	25 0	24 5	-0 5	2 0
D	12 5	10 7	-1 8	14 4
Composite of A,B,C, and D	29 2	29 0	-0 2	0 7

The relative standard deviation of this method is 4.2% (6)

[redacted]

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BIBLIOGRAPHY

1 J Brezina, Rec trav chim , 44, 520 (1925)

2 R W Foster and J H Cooper, "Analytical Methods for the Determination of Plutonium and Uranium in 'Scrup' Dissolver Solution", ORNL-1750, (In press)

3 H Hohn, Chemische Analyzen mit dem Polarographen, J Springer, Berlin, 1937, pp 51-52

4 A D Horton, Anal Chem 25, 1331 (1953)

5 A D Horton, Secret Notebook No 3209 pp 12, 22, Jan 11, 1954

6 Ibid pp 21, February 25, 1954

7 I M Kolthoff and J J Lingane, Polarography, 1st ed , pp 282-83, Interscience Publishers, Inc , New York, 1946

8 K A Kraus, G E Moore, and F Nelson, Chemistry Division Quarterly Report for Period Ending March 31, 1951, ORNL-1053, pp 19-21

9 G E Moore and K. A Kraus, J Am Chem Soc , 74, 843 (1952)

10 R L Pecsok, Anal Chem , 25, 561 (1953)

11 G Thanheiser and G Maassen, Mitt Kaiser-Wilhelm Inst Eisenforsch Düsseldorf, 19, 27 (1937)

[redacted]