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THE DETERMINATION OF IRON AND NICKEL IN
URANIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

Uranium has been analyzed for iron and nickel by atomic absorption spectrophotometry. Iron and nickel were determined in the samples under three different experimental conditions: 1. in solutions containing uranium, 2. in solutions extracted of uranium, and 3. by the method of additions. The results obtained are compared. A comparison is also made of results reported by atomic absorption, emission spectrography, and colorimetric methods.

The relative standard deviation for iron at 165 ppm was, by 1. 6.3%, 2. 4.3%, and 3. 7.9%. Relative standard deviation for nickel at 20 ppm was, by 1. 7.9%, 2. 2.8%, and 3. 36.0%. The ppm values are in terms of original uranium sample weight.

INTRODUCTION

The determination of iron and nickel in uranium is routinely accomplished by emission spectrography at Dow-Rocky Flats. On many samples, however, a check on these two impurities by an independent method is needed. The determinations are then usually made by a colorimetric method employing bathophenanthroline for iron and dimethylglyoxime-chloroform extraction for nickel.

There have been several papers¹⁻⁵ in the literature describing the determination of nickel and iron in a variety of matrices by atomic absorption spectrophotometry. The use of atomic

absorption for their determination in uranium could possibly offer an advantage in speed of analysis and in simplicity of method. An atomic absorption method might also be advantageous where there were elements present in the uranium that could cause interferences in the spectrophotometric methods. Examples of interfering elements being present are found in many uranium alloy analyses.

There are three rather general techniques employed to analyze solid samples by atomic absorption spectrophotometry. These are given in the first slide (Slide 1). The third technique could, if necessary, be used in conjunction with an impurity concentration step before the final determination. By testing all three of the techniques, a guideline for further work in atomic absorption analysis could be established.

EXPERIMENTAL

Instrumental

A Perkin-Elmer 303 Atomic Absorption Spectrophotometer was used for all analytical measurements. This is a double-beam instrument and was used with a 10 cm pre-mix acetylene-air burner. The instrumental parameters are given on the next slide (Slide 2).

The flame is slightly luminescent at these flow settings. It was found that this type of flame resulted in less electronic noise than the more air-rich flame sometimes used. Another small effect noticed was that the aspiration rate from sample solution containers held in the hand were affected by slight hand movements. A sample container support was therefore used in the analyses.

Standard Preparation

Master stock solutions of iron and nickel were prepared by the dissolution of iron and nickel oxides. Calculated amounts of Fe_2O_3 and NiO were dissolved in minimum amounts of 6 N HCl and brought to volume with distilled water. Dilutions of the master solution were made with 0.1 N HCl to prepare a series of standards covering the desired analytical range.

When samples containing uranium were analyzed, uranium was added to the standards to approximate the uranium concentration of the sample. In this way, any effects caused by the uranium in the sample should be compensated for by the uranium in the standards. Pure uranium oxide was used in preparing this uranium solution.

Sample Preparation

Samples of uranium metal weighing 2 grams each were dissolved in 6 N HCl and a small amount of HNO_3 . The solutions were evaporated to near dryness to remove HNO_3 . The residue was taken up and made to volume with 0.1 N HCl . Aliquots of the sample were then treated as needed for the method of analysis used. The solutions aspirated in the two techniques for analyzing uranium-containing solutions contained 1.6% uranium.

1. Direct method: Aliquots diluted to volume with 0.1 N HCl .
2. Method of additions: Three or more aliquots diluted to volume with 0.1 N HCl and spiked with known amounts of standard.

3. Separation method: Aliquots evaporated to dryness for total removal of HNO_3 , and taken up in concentrated HCl .

Separation of iron and nickel from uranium is accomplished in concentrated HCl as shown on the next slide (Slide 3). Cation exchange resin, Dowex 50, preconditioned with concentrated HCl , retains the iron. The effluent, containing nickel and uranium, is loaded on Dowex 1 anion exchange resin. Uranium is selectively absorbed by the anion resin allowing complete separation of the uranium and nickel. The effluent solution containing nickel is evaporated to near dryness, taken up and made to volume with 0.1 N HCl . Iron is eluted from the cation column into a beaker with 3 N HCl . The eluate is evaporated to near dryness, taken up and made to volume with 0.1 N HCl .

Recovery after separation for both iron and nickel has virtually been 100% from the HCl solution. However, any residual HNO_3 in the solution will lead to low iron recoveries. This is shown in the next slide (Slide 4).

RESULTS AND DISCUSSION

The analysis of synthetic uranium samples for nickel and iron indicated the methods were satisfactory. Several uranium samples were then obtained that had been analyzed by emission spectrography. Iron and nickel were determined in these samples by the three atomic absorption techniques. The samples were then independently analyzed by colorimetry for these elements. This resulted in each sample being analyzed by three different methods: emission spectrography, colorimetry, and atomic absorption. Three different intra-plant laboratories performed the analyses. This, as expected, gave three different answers for each element in the same sample.

The 1.6% uranium content of the uranium-containing solutions analyzed was found to be about optimum. The concentration of the nickel and iron at this dilution was in a good range for their determination, and the solution could be aspirated with little trouble. The analyzing of solutions containing over 2% uranium leads to burner clogging and a much higher electronic noise level.

Nickel

Uranium samples were analyzed for nickel by the three different atomic absorption techniques previously mentioned. The analytical curves were drawn from standards analyzed concurrently with the samples. The analytical curve for nickel in the uranium-containing solutions, shown in the next slide (Slide 5), was linear over the desired range. Nickel in the uranium-extracted solutions also gave a linear analytical curve, as shown on this same slide.

The amount of nickel in each sample was then determined by each of the techniques used. A comparison was made of these results which are shown in the next slide (Slide 6), and the results obtained by the other methods.

The possible interference effect of iron on the nickel results was investigated using a solution containing 20 ppm nickel and varying amounts of iron. The negligible effect of the iron on the nickel absorbance is shown in the next slide (Slide 7).

IRON

Analytical

The same uranium samples on which nickel determinations were made were also analyzed for iron. Analytical curves were drawn from standards analyzed concurrently with the samples. The analytical curve shown in the next slide (Slide 8) is linear over the desired range for the uranium-containing solution and also linear in the uranium-extracted solution.

The results obtained for iron by each of the three atomic absorption techniques are given in the next slide (Slide 9). The results by colorimetric methods and emission spectrography are again given for comparison.

When uranium-containing solutions of samples that had less than 50 ppm of iron were analyzed, it was found that the uranium contributed enough background noise to seriously mask the iron signal. For these samples, only the ion-exchange technique was used. Typical results are given on the next slide (Slide 10).

Precision

Precision data for nickel and iron were obtained by analyzing a routine uranium sample eleven times. Eleven portions of the metal were weighed and analyzed by the described methods. Relative standard deviations calculated are shown on the next slide (Slide 11).

The large R.S.D. calculated for nickel using the method of addition is caused by the relatively high noise level effect of the uranium to the small nickel signal at this level of concentration.

Ion Exchange Efficiency

The efficiency of the ion exchange method in removing most of the uranium from the analytical solutions was important for the analysis of U-235 enriched uranium. If a good separation could be obtained, the solutions could be aspirated into the burner using only the usual vent hood over the instrument. If not, radioactive contamination spread by the burner would make a special box necessary for the analyses.

Separation results obtained by the ion exchange procedure on sample solutions containing about 36 g/liter are given on the last slide (Slide 12). During a routine sample analysis, 10 mls of sample solutions are the most that would ordinarily be aspirated into the burner. Of this amount, only about 5% actually goes into the flame. By using the highest result for the amount of uranium remaining in the analytical solutions, less than 0.5 mg of uranium is discharged into the burner flame. A careful check with radiation detecting equipment did not reveal any significant contamination after analysis of a number of enriched uranium samples.

CONCLUSION

In conclusion, the following points have been brought out in this paper.

1. Iron and nickel can be determined in uranium by atomic absorption techniques with an accuracy comparable to that of colorimetric methods.
2. The use of an ion-exchange procedure makes possible the determination of iron in the <50 ppm (by weight) range. It also permits the safe analysis of enriched uranium samples without special equipment.

3. Of the three techniques used, the method of addition appeared to be not as accurate as the other two methods.

LIST OF SLIDES

<u>Slide Number</u>	<u>Description</u>
1	Techniques used in AA
2	Instrumental Parameters
3	Ion-exchange procedure
4	Effect of HNO_3 on ion exchange results
5	Nickel analytical curves
6	Comparison of Ni results
7	Effect of Fe on Ni results
8	Iron analytical curves
9	Comparison of Fe results
10	Results on low-iron samples
11	Precision
12	Ion-exchange efficiency

SLIDE 1

Determination of Elements by Atomic Absorption Spectrophotometry

1. Directly in the dissolved sample using prepared standards.
2. Directly in the dissolved sample using the method of addition.
3. Separation from the dissolved sample before final determination.

SLIDE 2

Instrumental Parameters

	<u>Nickel</u>	<u>Iron</u>
Wavelength - A	2320	2483
Lamp Current - ma	25	40
Slit Width - mm	0.3	0.3
Scale Expansion	X5	X5
Air Flow (Flowmeter Reading)	9.25	9.25
Acetylene Flow (Flowmeter Reading)	9.50	9.50

SLIDE 3

Separation of Iron and Nickel from Uranium

Sample in Conc. HCl

Dowex 50 (+)

3N HCl

Fe

Dowex 1 (-)

Ni

SLIDE 4

Effect of HNO_3 on Ion-Exchange
Iron Results for Same Sample

<u>Sample</u>	<u>Weight, grams</u>	<u>Iron Found, ppm</u>
U + HCl	0.4696	177
U + HCl	0.4248	173
U + HCl	0.4258	171
U + HCl + HNO_3	0.4525	157

NICKEL ANALYTICAL CURVES

SLIDE 6

A Comparison of Nickel Results by Different
Analytical Methods

<u>Sample Number</u>	<u>Atomic Absorption Techniques, ppm Ni</u>			<u>Colorimetric ppm Ni</u>	<u>Emission Spectrographic ppm Ni</u>
	<u>Uranium Extracted</u>	<u>Uranium Present</u>	<u>Method of Addition</u>		
1	39	34	37	41	35
2	32	26	41	30	30
3	37	26	39	38	30
4	34	21	36	59	30
5	27	20	36	35	20

SLIDE 7

Effect of Iron on Nickel Results

Amount of Element Present		Absorption
<u>Nickel, ppm</u>	<u>Iron, ppm</u>	<u>Reading</u>
20	0	0.040
20	10	0.039
20	20	0.040
20	40	0.039
20	80	0.039
20	120	0.038

IRON ANALYTICAL CURVES

SLIDE 9

A Comparison of Iron Results by Different Analytical Methods

<u>Sample Number</u>	<u>Atomic Absorption Techniques, ppm Fe</u>			<u>Colorimetric ppm Fe</u>	<u>Emission Spectrographic ppm Fe</u>
	<u>Uranium Extracted</u>	<u>Uranium Present</u>	<u>Method of Addition</u>		
1	206	265	394	221	170
2	213	228	244	188	130
3	148	175	232	161	150
4	63	43	118	49	40
5	190	184	255	188	130

SLIDE 10

Results on Uranium Samples Containing
Low Amounts of Iron

<u>Sample Number</u>	<u>Atomic Absorption Uranium Extracted</u>	<u>Colorimetric</u>
1	30	20
2	24	27
3	26	31
4	21	26

SLIDE 11

Analytical Precision for Nickel and Iron

<u>Element</u>	<u>Amount Present</u>	<u>Relative Standard Deviation</u>			<u>Method of Additions</u>
		<u>U-Containing</u>	<u>U-Extracted</u>		
Nickel	20 ppm	7.9 %	2.8 %	36	%
Iron	165 ppm	6.3 %	4.3 %	7.9	%

SLIDE 12

Ion-Exchange Removal of Uranium

<u>Amount Uranium in Original Solution</u>	<u>Sample Number</u>	<u>Uranium Remaining After Ion Exchange g/liter</u>
36 g/liter	1	0.75
	2	0.42
	3	0.59
	4	0.38
	5	0.46

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