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THE DETERMINATION OF NICKEL IN ZIRCONIUM WITH DIMETHYLGLYOXIME

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ABSTRACT

A colorimetric method is presented for the determination of microgram quantities of nickel in zirconium metal with dimethylglyoxime. The zirconium metal is dissolved in dilute HF. Citric acid is added to complex the zirconium. Nickel is oxidized with bromine water. A large excess of ammonium hydroxide is added. The solution is cooled below room temperature and dimethylglyoxime is added. After approximately fifteen minutes, the optical density of the solution is measured at 540 mμ. Interferences are negligible. Results are given and are shown to be comparable to those obtained polarographically. The color is stable for at least three hours but results are better if the optical density is measured after a definite length of time.

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I. Introduction.

A direct colorimetric method for the determination of nickel in zirconium metal has been requested. The method adopted is based on the reddish-brown color produced when tetravalent nickel reacts with dimethylglyoxime. The conditions are essentially those established by Pieters, Hanssen and Geurts (1) wnen determining nickel in iron. Slight modifications to further reduce errors due to interfering elements by using a narrow band as obtained by the Beckman spectrophotometer in place of a filter photometer have been made.

II. Discussion.

Pieters et al (1) have succeeded in stabilizing the color of nickelic dimethylglyoxime, produced by bromine oxidation, by using a large excess of ammonium hydroxide. Consequently, the principal disadvantage of the method was overcome.

Pieters et al report that the principal interfering elements are Co, Fe, and Cr. In their work, however, they used a filter photometer with the center of the band width at approximately 520 mμ. When using a Beckman spectrophotometer with a 1 mμ band width at 538 mμ, the interference due to Fe and Cr is completely eliminated. They also report that Co interferes to

the extent of about 20% when present in a 10 to 1 ratio of Co to Ni. Since, however, only negligible quantities of cobalt have been found in the present zirconium production, the possibility of appreciable interference is neglected.

The sample is dissolved in dilute HF. Citric acid is added to complex the Zr, Al, Fe, etc., Bromine is used as the oxidizing agent. The solution is neutralized and an excess of ammonium hydroxide is added. The color is developed with dimethylglyoxime and its optical density is measured at 538 mμ, using a Beckman Spectrophotometer, 1 to 2 mμ band width and 1 cm cells.

III. Experimental.

Pieters et al (1) report the use of concentrated NH_4OH while in a separate part of the paper, NH_4OH of density 0.95 is specified. The latter concentration corresponds to a more dilute solution and when used in the quantity suggested, a stable color is not established when determining nickel in zirconium. If, however, concentrated NH_4OH is used in the same volume, a color which is nearly stable for at least three hours is produced. This is shown in Table 1.

Table 1.

STABILITY OF THE NICKELIC DIMETHYLGLYOXIME COMPLEX

0.5 g Zr/100 ml containing 5 ml excess conc. NH_4OH. Measurements made at 540 mμ using 1 cm cells.

	Optical Density			
γ Added Ni	15 min.	25 min.	60 min.	180 min.
50	.059	.061	.062	.062
100	.117	.118	.123	.128
150	.174	.178	.186	.188
200	.227	.235	.246	.258
250	-	-	.293	.303

The method does not work well when more than 200 γ (≡ 400 ppm) of Ni are present. A precipitate forms and the nickelic dimethylglyoxime color complex is produced but slowly.

The color due to the ferric citrate complex is known not to interfere at wave lengths above about 500 mμ (2). The interference due to chromium as a chromate is also known to be negligible at 538 mμ (3). The possibility of chromium forming a color with dimethylglyoxime that might interfere at this wave length was investigated. No interference was detected due to chromium in varying amounts up to 500 ppm.

Inasmuch as the available standard zirconium samples (NBL 284 or NBL 285) were known to contain but little nickel, resort was made to other less positive means for determining the accuracy of the method. Samples were analyzed

for nickel which had previously been analyzed polarographically (4). A standard zirconium sample (NBL-285) was spiked with known quantities of nickel. Analysis of the spiked sample and three unknowns containing appreciable iron, chromium and nickel are shown in Table II.

Table II

COMPARISON OF COLORIMETRIC AND POLAROGRAPHIC METHODS

0.500 gm. samples of Zirconium Metal

Sample No.	Ni Added-ppm	Ni Found - ppm Polarograph	Colorimetric
285	300	290	300
6121	0	65	68
6125	0	140	153
6127	0	310	350

IV. Procedure

1. Weigh a 0.500 gm sample of Zr metal into a 100 ml platinum or bakelite beaker.
2. Completely dissolve the sample in 10 ml of H_2O plus 1 ml of 48% HF.
3. Add 10 ml of 10% citric acid, 5 ml of saturated Br_2 water, and about 5 ml of saturated boric acid (0.85M).
4. With stirring, add concentrated NH_4OH until the color just disappears. Then add 5 ml in excess.
5. Transfer the solution to a 100 ml volumetric flask and cool to slightly below room temperature.
6. Add 3 ml of 0.1% dimethylglyoxime in alcohol.
7. Approximately 15 minutes after adding the dimethylglyoxime, dilute the solution to volume. Read the optical density of the solution in a 1.00 cm cell at 540 mμ.
8. Obtain the concentration in ppm by reference to a standard calibration curve.

SUMMARY

The dimethylglyoxime method for the determination of nickel has been applied to the analysis of zirconium samples. A stable color has been established after bromine oxidation. Results are accurate when determining amounts of nickel to about 200 γ.

Bibliography

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