*Ultraviolet Spectrophotometric Determination of Nickel with α-Benzildioxime**

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α-Benzildioxime was first used by Tschugaeff1) for the detection of nickel. The reagent was further studied by Atack and others for its estimation2,3). Though this reagent is superior to dimethylglyoxime as a precipitant of nickel, very few methods have been hitherto proposed for the colorimetric as well as spectrophotometric determination of microgram quantities of the element, the dimethylglyoxime method being thus still widely utilized4).

In the present paper a sensitive spectrophotometric method for determining nickel with α-benzildioxime is proposed. This method comprises extraction of the nickel (II) chelate compound with chloroform and subsequent photometric measurement in the ultraviolet region. Recently, Ni (II)-α-furildioxime in 1, 2-dichlorobenzene5) and also Ni (II)-dimethylglyoxime in chloroform6) have been recommended as colored complexes suitable for the direct determination of nickel. However, because of the higher sensitivity of its colored system, the present procedure seems to have some advantage over these two methods.

The absorbance readings for the determination have been carried out at the wave lengths of 275, 358, and 406 mμ. The characteristic absorption maximum at 275 mμ is more sensitively measured than those at 358 and 406 mμ. On account of intense spectral absorption of α-benzildioxime itself in the ultraviolet region, the absorbance reading at 275 mμ can not be performed unless the excessive reagent is completely eliminated from the solvent. The present method is available for the determination of nickel in the presence of copper.

Reagent and Apparatus

The stock solution of nickel was prepared by dissolving 4.805 g. of nickel sulfate heptahydrate in 0.1 N sulfuric acid and diluted with the same to 1 liter. An aliquot of this solution was again diluted with 0.1 N sulfuric acid and the resultant solution containing 2 μg. of nickel per ml. served as standard.

The α-benzildioxime 0.02% solution was prepared by dissolving 0.02 g. of the reagent in 100 ml. of a mixture of ethyl alcohol and concentrated ammonia (95 to 5 by volume).

Redistilled chloroform was used for extraction and sodium tartrate or citrate 10% solution for preventing the precipitation of ferric hydroxide.

Glass stoppered test tubes (20 mm. × 150 mm.) and a shaking apparatus (200 cycles per minute) were most conveniently utilized for extraction and washing.

All absorbance readings were made with a Beckman Model DU spectrophotometer equipped with 1 cm. quartz cells.

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1) L. Tschugaeff, *Z. anorg. Chem.*, **46**, 144 (1905).

2) F.W. Atack, *Analyst*, 38, 316 (1913); *C.A.*, 7, (1913); *J. Chem. Soc.*, **1913**, 103 1317.

3, 7) Frank J. Welcher, "Organic Analytical Reagents", Vol. III., D. Van Nostland Company, Inc. New York, 1947, pp. 224-7; W.F. Hillebrand, G.E.F. Lundell, H.A. Bright, J.I. Hoffman, "Applied Inorganic Analysis", 2nd Ed., John Wiley & Sons, Inc., New York, 1953, pp. 411-2.

4, 9) E.B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd, Ed., Interscience Publishers, Inc., New York, (1950) pp. 469-74.

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Absorption Spectra of α-Benzildioxime and its Nickel Chelate in Chloroform

Nickel compound was precipitated according to the procedure described to the ordinary analytical method⁷⁾ and recrystallized from chloroform. It was dissolved in chloroform and subjected to the spectral measurements at the wave lengths between 250 and 500 mμ. Three distinct absorption bands of the chelate appeared at λ=275, 358, and 406 mμ, among which the band at 275 mμ was most pronounced in intensity⁸⁾.

In Fig. 1, curve 1 shows the absorption spectrum of nickel chelate obtained by the extraction process. In the region shorter than 300 mμ there appears a continuous absorption. This is obviously due to the intense absorption of the excessive reagent transferred to the chloroform layer during the extraction. However, the absorption curve showed a maximum at 275 mμ when the chloroform solution was washed with a dilute sodium hydroxide solution (curve 2). Curves 3 and 4 represent the absorption spectra of α- benzildioxime before and after being washed with sodium hydrodroxide. From these observations it was made clear that the excessive reagent transferred frkm the aqueous solution into the chloroform layer can be almost entirely removed by washing.

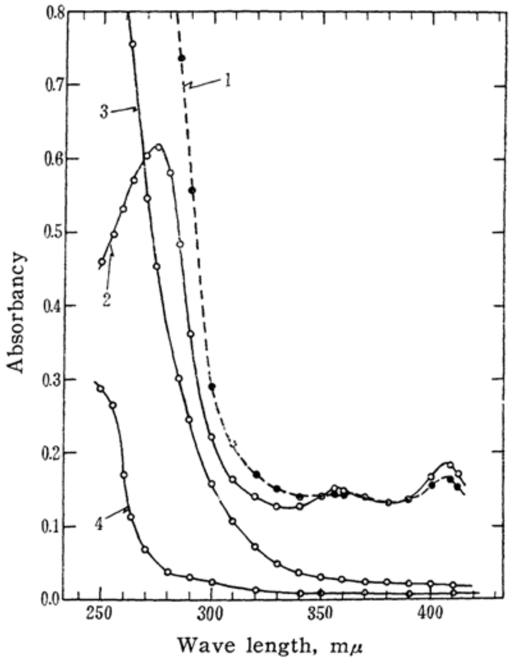

Fig. 1. Absorption spectra of α-benzildioxime and its nickel (II) chelate in chloroform.
1: Ni chelate, 0.8 p.p.m. as nickel, 2: Ni chelate washed with dil. NaOH, 0.8 p.p.m. as nickel, 3: α-benzildioxime, 4: α-benzildioxime washed with dil. NaOH.

Absorption Spectra of Copper (II) and Cobalt (II) combined with α-Benzildioxime

Copper was found to be also transferred to the chloroform phase to a great extent in the said extraction process which certainly caused an interference in the estimation of nickel. This interference was nearly obviated, however, since a striking color change from brown to yellow took place when the liquid was shaken with a dilute sodium hydroxide solution. Further elimination of the copper from the chloroform phase could be made if the chloroform phase was shaken with dilute ammonia. In case of the dimethylglyoxime method⁹⁾ copper may be entirely removed from the chloroform extract when shaken with dilute ammonia. However, the removal of copper α-benzildioxime from the chloroform phase is not satisfactory if the extract is washed only with ammonia.

Cobalt is also transferred to the chloroform phase in the extraction process, and the interference of this metal could not be simply eliminated by washing with sodium hydroxide solution and ammonia. These effects are shown in Fig. 2 and are summarized as follows:

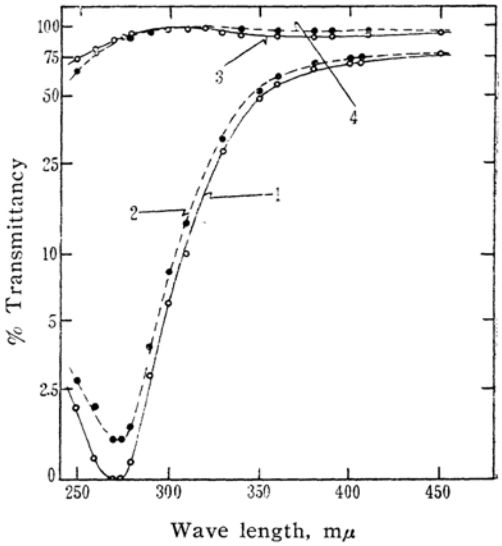

Fig. 2. Absorption spectra of copper with α-benzildioxime in chloroform.
1: copper in original extract, 2: washed with dil. ammonia, 3: washed with dil. NaOH, 4: washed with dil. NaOH, then with dil. ammonia.

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8) K. Sone, *J. Am. Chem. Soc.*, 75, 5207 (1953).

Metal,	Color in chloroform,	Color after washing		
		with NH_4OH,	with NaOH,	with NaOH then NH_4OH
Ni–complex	yellow	yellow	yellow	yellow
Cu–complex	brown	brown	yellow	colorless
Co–complex	yellow	yellow	yellow	yellow

From these experimental results it was confirmed that the positive error due to the presence of copper is most effectively minimized by washing the chloroform extract first with a dilute sodium hydroxide solution and then with dilute ammonia.

Fig. 3 indicates that by this treatment the absorption of the copper compound becomes almost negligible in the region longer than 300 mμ whereas the band due to cobalt whose maximum is 260 mμ still predominates. This fact suggests to us that the present procedure allows us to estimate nickel in the solution which contains a certain amount of copper but no cobalt.

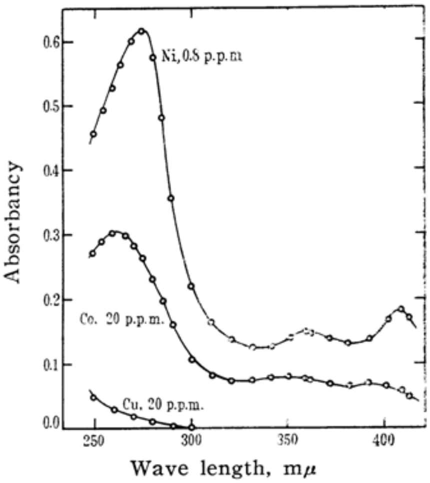

Fig. 3. Absorption curves of nickel, cobalt, and copper.

Conditions for Color Development and Extractions

Effect of pH.—Completeness of precipitation and extractability with chloroform using buffer solutions with pH ranging from 6.0 to 11.4. The optimum pH for the extractions was found to be 8.8 or above. When pH of the solution exceeds 8.8 the nickel complex precipitates immediately, allowing the extraction to be carried out rapidly. This fact shows that the strict adjustment of pH is not necessary, thus eliminating the use of a buffer.

Duration and Number of Extractions.—In order to determine the duration of extraction a series of solutions containing a definite amount of nickel were extracted by shaking the containers mechanically with a shaking apparatus (200 cycles per min.) for some time. Data in Table I show that the duration of two minutes is sufficient for removing the complex from the aqueous solution provided that 5 ml. of chloroform is used. Complete removal was confirmed by the absence of the spectral absorption due to the nickel chelate in the second chloroform extract. When the volume of the aqueous solution was 5 to 50 ml., complete extraction was established by shaking with 5 ml. of chloroform for two minutes.

TABLE I

EFFECT OF DURATION ON EXTRACTION

Duration, min.	Absorbancy 358 mμ	Absorbancy 406 mμ
2	0.666	0.740
5	0.668	0.744
10	0.666	0.744
15	0.666	0.744

Aqueous volume, 15 ml. Nickel taken, 20 μg. Organic solvent, 5 ml. of chloroform at a time.

Amount of Reagent. — The solubility of α-benzildioxime in ethyl alcohol is about 0.2 g. per liter, which increases to some extent in ammoniacal medium. In the present method the reagent solution of 0.02% was prepared, 2 ml. of which was required to extract 20 μg. of nickel (theor. mole ratio of the reagent for nickel was 1 : 2.5) this was the maximum concentration (4 p. p. m. in chloroform) available in this determination. Although up to 4 ml. the reagent was found to give no effect on the absorbancy of the nickel chelate in the measurements at 358 and 406 mμ, 2 ml. was used lest the reagent should make any disturbance. Since the absorption, especially at 275 mμ, due to α-benzildioxime itself, was intense the use of more of the reagent must be avoided.

General Procedure

Isolation of Nickel.—To about 15 ml. of slightly acidic sample solution in a glass stoppered test tube, containing up to 20 μg. of nickel, add 2 ml. or more of 10% sodium tartrate or citrate solution to prevent the precipitation of hydroxide of ferric iron. Make the solution ammoniacal by adding 2 ml. of 10% ammonia or a few drops of concentrated ammonia in excess, add 2 ml. of 0.02% α-benzildioxime solution, and shake the tube for ten seconds by hand. As red precipitate appears immediately, add exactly 5 ml. of chloroform with a pipet. Shake the tube for two minutes horizontally with a shaking apparatus (200 cycles per min.), and extract the precipitate.

Washing. — Draw off the aqueous layer by suction, introduce 10 ml. of 1% sodium hydroxide solution into the tube, and shake the tube for one minute as before. Draw off the alkaline layer by suction, and wash the chloroform layer once with 10 ml. of 0.5% ammonia, then with two 10 ml. portions of 1% sodium hydroxide solution for one minute successively.

Photometric Determination of Nickel.—After the last washing liquid is nearly completely removed, the chloroform solution is taken up with a dry pipet and filtered into a 1 cm. quartz cell using dry filter paper of small size. Prepare a blank reagent solution by introducing about 15 ml. of distilled water into the tube and treating the water by the same procedure. The standard nickel solutions prepared for setting up the calibration curves should be also treated by the same procedure as the sample solution. Make the absorbance measurements for the chloroform solutions of the sample, standard, and reagent blank at 275, 358, or 406 mμ respectively, pure chloroform being put in the reference cell. Subtract the absorbancy of the reagent blank from that of the sample as well as the standard, and determine the amount of nickel in the given sample. Fig. 4 gives the calibration curves for nickel at 275, 358, and 406 mμ. As shown in Fig. 4 and Table II, the maximum sensitivity on the present spectrophotometric method is attained when the absorbance readings at 275 mμ are used. The sensitivity is superior to that of he classical dioxime method.

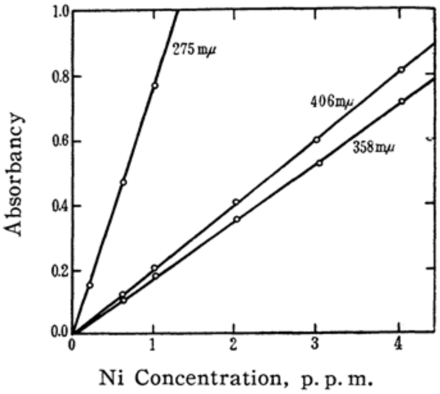

Fig. 4. Calibration curves for nickel. Beckman Model DU spectrophotometer, with 1 cm. quartz cells.

TABLE II

SENSITIVITY FOR α-BENZILDIOXIME METHOD (Solvent, chloroform)

Ni taken,	Ni, p. p. m./($A_s \times 10^3$)(b)		
p. p. m.(a)	275 mμ	358 mμ	406 mμ
0.2	1.31×10^{-3}	5.56×10^{-3}	4.76×10^{-3}
0.4	1.33 〃	5.55 〃	4.88 〃
0.6	1.29 〃	5.56 〃	4.92 〃
1.0	1.31 〃	5.59 〃	4.74 〃
2.0		5.62 〃	4.95 〃
4.0		5.59 〃	4.95 〃
Average	1.31 〃	5.59 〃	4.94 〃

(a) Microgram of nickel per ml. of chloroform.

(b) Sensitivity, by Sandell's definition[10]. A_s, absorbancy.

Influence of Foreign Ions

By observing the conditions prescribed above better extractability and stability of the complex are attained thusall owing much more satisfactory separation of nickel from ferric iron, aluminum, zinc, chromate, vanadate, and molybdate ions. In Table III the results for the determination of nickel in the presence of ferric iron and other interfering elements such as copper and cobalt are shown. This table shows that when as much as 5 μg. of nickel is to be determined the allowable concentration for copper is as high as 0.1 mg. and for cobalt 0.01 mg.

As already discussed copper is readily extracted into the chloroform phase from which it is eliminated by washing with sodium hydroxide solution and ammonia. In case where its concentration is higher than 0.1 mg., however, copper may hinder nickel from reacting with the reagent (expt. Nos. 4 and 5 in Table III). Therefore, if the concentration of copper should be much higher than that of nickel, the amounts of the reagent as well as chloroform must be increased.

TABLE III

EFFECT OF COPPER, COBALT, AND IRON ON THE DETERMINATION OF NICKEL

No.	Foreign ion added, mg.		Ni found, μg.		
			275 mμ	358 mμ	406 mμ
1	0.01	Cu	5.0	5.0	5.0
2	0.05	〃	5.1	5.1	5.0
3	0.1	〃	5.4	5.1	5.2
4	0.5	〃	1.0	1.0	0.7
5	1.0	〃	1.2	1.2	0.8
6	0.005	Co	4.9	5.0	5.0
7	0.01	〃	5.1	4.9	5.0
8	0.05	〃	5.5	5.5	5.6
9	5.5	Fe (III)	5.1	5.0	5.0
10	11.0	〃	5.1	5.0	5.0

Ni taken in 10 ml. of aqueous solution, 5.0 μg. 10 % sodium citrate solution added, 4 ml. Reagent solution added, 2 ml. Chloroform, 5 ml.

TABLE IV

REPRODUCIBILITY OF DETERMINATION OF NICKEL IN SYNTHETIC SOLUTION

Ni found, absorbancy,			Deviation from Av. absorbancy		
275 mμ	358 mμ	406 mμ	275 mμ	358 mμ	406 mμ
0.755	0.181	0.212	0.019	0.003	0.004
0.783	0.184	0.216	0.009	0.000	0.000
0.780	0.178	0.217	0.006	0.006	0.001
0.775	0.180	0.216	0.001	0.004	0.000
0.785	0.189	0.217	0.011	0.005	0.001
0.770	0.188	0.214	0.004	0.004	0.002
0.768	0.187	0.218	0.006	0.003	0.002
Av. 0.774	0.184	0.216			
Av. deviation			0.0080	0.0036	0.0014
Max. deviation			0.019	0.006	0.004
Av. relative deviation			1.03%	1.96%	0.65%
Max. relative deviation			2.45%	3.26%	1.85%

Composition of the synthetic solution, Fe (III) 54.5%, Cu (II) 1.0%, Cr (VI) 1.1%, Al 32.7%, Mo (VI) 4.4%, V (V) 0.7%, Zn 5.5%, Ni 0.1%.

Total amount of elements, 5.0 mg. in 10 ml.

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[10] E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., Intersince Publishes, Inc. New York, 1953, p. 49.

In order to test the precision of the method, the determination was made with the synthetic solution which contained ferric iron, aluminum, zinc, chromate, vanadate, molybdate, copper, and nickel ions whose total amount was 5.0 mg. The absorbance readings of seven determinations showed average and maximum relative errors to be 1.03 and 2.45% at 275 mμ, 1.96 and 3.26% at 358 mμ, and 0.65 and 1.85% at 406 mμ respectively. These are shown in Table IV.

Summary

A new method described here involves the extraction of nickel (II)-benzildioxime with chloroform and the spectrophotometric measurements of the colored system in the same solvent. The wide pH range for the extraction eliminates the use of a buffer, and nickel is readily separated from ferric iron, aluminum, zinc, chromate, vanadate, and molybdate ions. By obviating the excessive benzildioxime with dilute alkali, the most sensitive absorbance readings are achieved, and the sensitivity at 275 mμ is 0.0013. Beer's law holds up to 1 p. p. m. of nickel at 275 mμ, and up to 4 p. p. m. at 358 and 406 mμ. The nature and degree of interference of copper and cobalt on the color development are also discussed, and their allowable amounts are determined.

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