

Spectrophotometric Determination of Nickel by Mineral Acid

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The spectrophotometric determination of nickel was studied by using various mineral acids such as hydrochloric, perchloric and sulfuric acid as reagents. The absorption spectra were measured in detail for the cobaltous perchlorate at various concentrations of each acid solution and it was found that the spectra were quite similar in the cases of perchloric acid and sulfuric acid solution. This was attributed to the existence of cobaltous aquo ion. In the hydrochloric acid medium, the spectra were more complicated, showing bathochromic and hyperchromic effects as the increase of the concentration of the hydrochloric acid, and the result was ascribed to the successive formation of chloro-complexes. The calibration curves for cobalt were made at appropriate wave lengths in each acid solution and Beer's law was obeyed in the range of $0.05M$ — $0.3M$. The proposed method for the determination of cobalt is simple in procedure but has a low sensitivity.

The spectrophotometric method for the determination of metal using mineral acid has the merits of good accuracy and simplicity in the procedure because no special reagent such as organic reagent is needed. Several works have recently been reported on the methods by the mineral acids such as hydrochloric, hydrobromic, sulfuric and perchloric acid¹⁻⁸⁾. In these methods, the absorbance of the solution was measured at maximum wave length of absorption band which may be due to the complexes formed between the metallic ions and the anions such as sulfate, hydroxyl, chloride and acetate ions. In order to establish a series of the spectrophotometric determinations of metallic ions, we have already reported the methods for determining iron, lead, bismuth in which sulfuric, perchloric, hydrochloric and acetic acids were used as the reagents⁹⁻²⁰⁾.

The present paper reports the study on the absorption spectra of nickel salt in aqueous solution and the determination of nickel using various acids such as HCl, HClO₄, H₂SO₄ etc.

APPARATUS AND MATERIALS

Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer, Model DU, with 1 cm corex cells.

The stock solution of nickel was prepared as follows. Nickel perchlorate was prepared by dissolving proper amounts of electrolytic nickel in perchloric acid (about 4 N) and evaporating the solution until the formation of crystals was observed. After perchloric acid was added to dissolve the deposit, the solution was evaporated

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again. The procedure was repeated until the solution gave negative test for chloride. The pale green crystals separated on cooling were filtered with a sintered glass filter and recrystallized twice from distilled water. A stock solution of nickel ($0.500M$) was prepared by dissolving the crystals of nickel perchlorate in water. All of the solutions for absorbance measurements were prepared by diluting the required quantity of the stock solution.

All other reagents used such as hydrochloric, sulfuric and perchloric acids were analytical grade.

EXPERIMENTAL

Absorption Spectra

The absorption spectra of nickel perchlorate in various media such as aqueous, perchloric, sulfuric, acetic and hydrochloric acid solution are shown in Fig. 1. The concentrations of the acids were held constant at 6 *N*. All of the spectra show four absorption maxima, and these wave lengths and their molar extinction coefficients

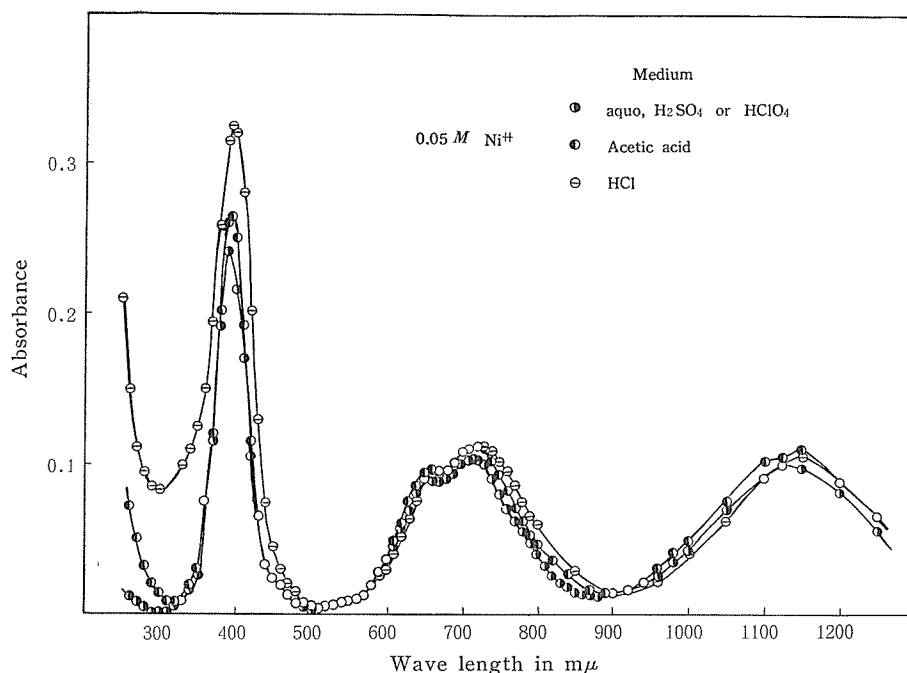


Fig. 1. Absorption spectra of nickel solution.

were represented in Table 1. The absorption spectra in perchloric acid and sulfuric acid are quite similar to that in aqueous solution and are ascribed to the presence of the nickel aquo-ion. In acetic and hydrochloric acid media, however, the absorbance increases and the absorption maxima shift to longer wave lengths. Such bathochromic and hyperchromic effects are more remarkable in hydrochloric acid medium. Therefore the effect of change in the concentration of this acid was studied.

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Table 1. Absorption maxima of nickel solution.

Nickel solution	Max. wave length in $m\mu$ (Molar extinction coeff.)			
$Ni^{++}-H_2O$	394(4.72)	650(1.80)	718(2.06)	1130(1.94)
$Ni^{++}-4.8N\ HClO_4$	394(4.72)	650(1.80)	718(2.06)	1130(1.94)
$Ni^{++}-6N\ HCl$	396(6.52)	670(1.96)	730(2.26)	1150(2.08)
$Ni^{++}-6N\ H_2SO_4$	394(4.72)	650(1.80)	718(2.06)	1130(1.94)
$Ni^{++}-6N\ CH_3COOH$	394(5.30)	654(1.96)	720(2.13)	1150(2.16)

Fig. 2 shows the spectra of nickel perchlorate in solution of various concentrations of hydrochloric acid. The absorption maxima shift to the longer wave length in the region of near ultraviolet, and the absorbance in these bands increases with the increase of the concentrations of the acid. In the region of 600~800 $m\mu$, the absorbance also increases, and the change is more remarkable. In order to investigate the effect of chloride concentration, absorption spectra were measured under the constant acidity.

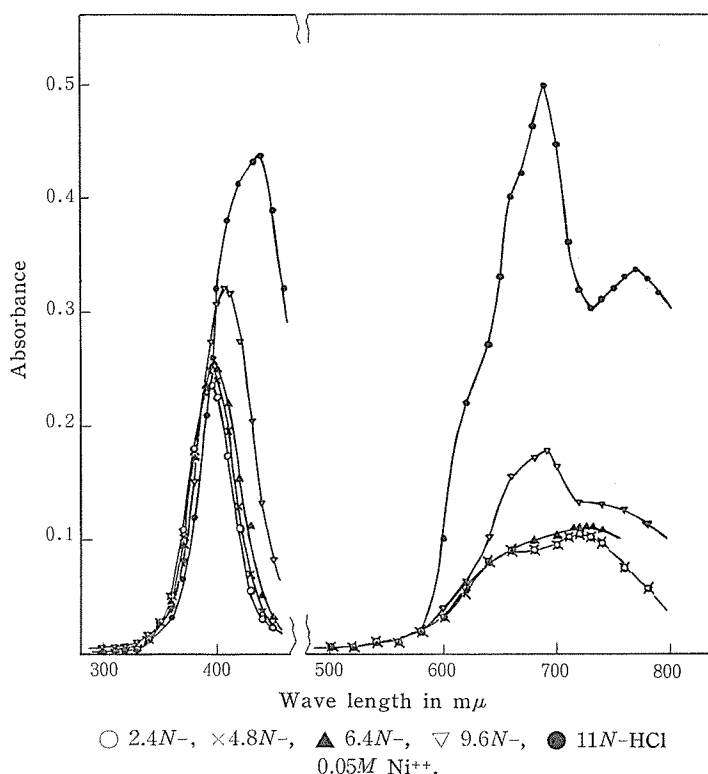
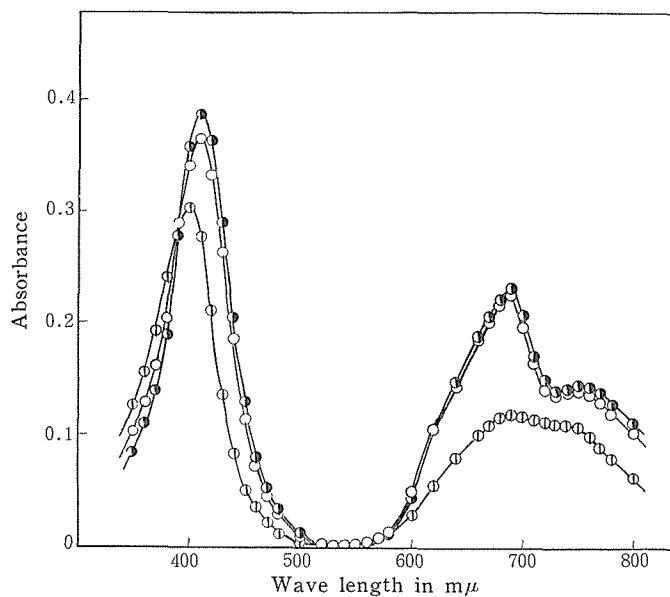


Fig. 2. Absorption curves of nickel solution at various hydrochloric acid concentration.

The spectra obtained in 9.6 N hydrogen ion, are shown in Fig. 3, as an example. The changes of the absorption curves shown in Fig. 3 are similar with that in Fig. 2, and this might be due to the stepwise formation of nickel chloro-complex.



● 4.8M-, ○ 2.4M-, □ 0.48M- Cl⁻. 0.05M Ni⁺⁺, 9.6M H⁺
Fig. 3. Absorption curves of nickel solutions at various chloride concentration.

Determination of Nickel

Nickel aquo-complex and nickel chloro-complex are used for the determination of nickel. From the above experiments it is concluded that for the determination of nickel, any acids except hydrochloric acid may give the same results as the reagent. Calibration curves, therefore, were made in the media of perchloric and hydrochloric acids, respectively. The results were shown in Figs. 4 and 5. In both cases, the Beer's

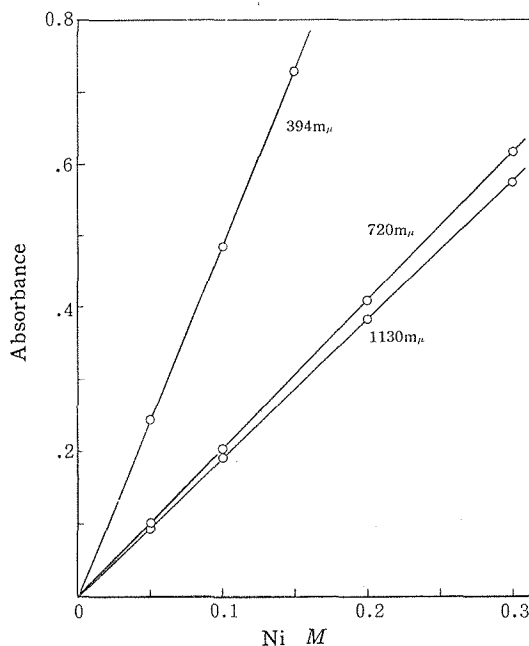


Fig. 4. Calibration curves for nickel-aquo method.

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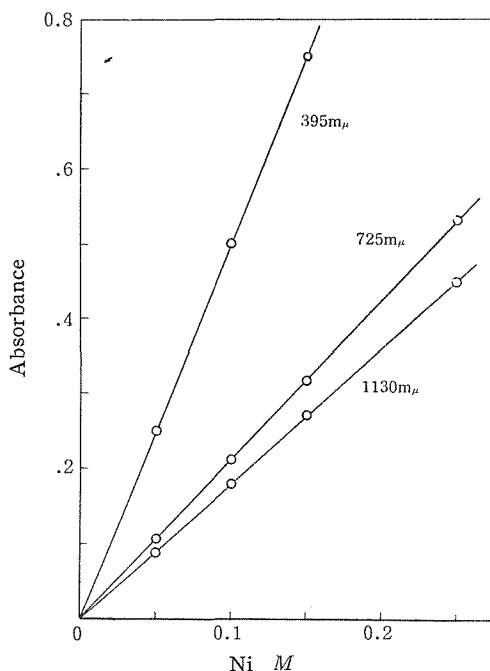


Fig. 5. Calibration curves for nickel-chloride method.

law is followed up to $0.3 M$. From the preliminary survey mentioned above, the measurements must be made under the constant concentration of hydrochloric acid in the latter. In this case, the concentration of hydrochloric acid was held constant at $6 N$. But in the former, such consideration is not required. These analytical results may be applied to the simultaneous determination of iron, cobalt and nickel.

SUMMARY

The method of spectrophotometric determination of nickel by mineral acid was studied. The absorption spectra were obtained in various medium in detail for the first time. The maxima were found at 394 , 650 , 718 and $1130 m\mu$ in both cases of perchloric acid and sulfuric acid solutions, but these bands shifted to longer wave lengths in hydrochloric and acetic acid solutions and also this bathochromic and hyperchromic effects became more remarkable with the increase of the concentration of the acids. The above observations may be attributed to the successive formations of chloro- or acetato-complexes.

The calibration curves were made at each maxima under the constant concentration of the above acids and Beer's law was obeyed in the range of $0.05 \sim 0.3 M$ in all cases. The proposed method may be effectively applied to determine the amounts of nickel in considerable concentrated solution by simple procedure.

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