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Determination of Cobalt and Nickel by Graphite-Furnace Atomic Absorption Spectrometry after Coprecipitation with Scandium Hydroxide

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Trace amounts of cobalt and nickel in a water sample were quantitatively coprecipitated with scandium hydroxide at pH 8.0 - 10.5. Because the coprecipitant could be easily dissolved with 1 mol dm⁻³ nitric acid, and the presence of up to 10 mg cm⁻³ of scandium did not interfere with the graphite-furnace atomic absorption spectrometric determination of cobalt and nickel, the volume of the final solution prepared for the determination could be minimized down to 0.5 cm³. The concentration factor was 400-fold and the detection limits (signal to noise = 2) were 5.0 pg cm⁻³ of cobalt and 10.0 pg cm⁻³ of nickel in 200 cm³ of the initial sample solution. The 27 diverse ions investigated did not interfere with the determination in at least a 500-fold mass ratio to cobalt or nickel. The proposed method was successfully applied to the determination of trace amounts of cobalt and nickel in river-water samples.

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The coprecipitation method is useful for the concentration of trace metal ions, and has often been combined with graphite-furnace atomic-absorption spectrometry for the determination of the trace metal ions. In a previous paper,¹ we proposed scandium hydroxide as an excellent coprecipitant for some metal ions, such as copper, lead, and cadmium, because of its good collecting ability and ease of dissolution in dilute mineral acids, and demonstrated the determination of a trace amount of copper using graphite-furnace atomic absorption spectrometry combined with the scandium coprecipitation technique. This time, we found that scandium hydroxide is also a good coprecipitant for trace amounts of cobalt and nickel, and that the coprecipitated metal ions can be determined satisfactorily by graphite-furnace atomic absorption spectrometry, even under the presence of a large amount of scandium. Since scandium hydroxide could be easily dissolved in dilute nitric acid, the final sample volume prepared for the determination could be minimized down to 0.5 cm³, and hence the concentration factor of cobalt and nickel reached 400-fold. The method proposed here is simple and reproducible.

Until now, a variety of coprecipitants have been proposed for the concentration of both cobalt and nickel prior to the determination by graphite-furnace atomic absorption spectrometry.²⁻⁹ However, a method using zirconium hydroxide² requires heating to dissolve the coprecipitant, and the use of tin(IV) hydroxide³ makes it necessary to be allowed to stand the final solution overnight to remove the tin carrier. The use of iron(III) tetramethylenedithiocarbamate requires a long digestion of the precipitate in order to simplify the sample matrix,⁴ or destroying the scum obtained by the flotation technique.⁵ Although indium hydroxide^{6,7} is an excellent collector, indium itself causes serious background absorption. To eliminate background absorption, therefore, the minimization of the indium amount⁶ and the volatilization of indium as bromide during the ashing stage⁷ were tried. Although magnesium oxinate⁸ is also an effective collector,

precipitation should be encouraged by heating when seawater is analyzed. Ammonium pyrrolidinedithiocarbamate (APDC) of copper and iron⁹ is dissolved only slowly.

For the preconcentration of cobalt alone, magnesium 8-quinolate¹⁰ and nickel 8-quinolinol/1-nitroso-2-naphthol complex¹¹ have been proposed, giving extremely high concentration factors. In these methods, the coprecipitates are submitted to analysis without dissolution. Also, in the use of disulfide¹² for cobalt collection, the suspension of the coprecipitate is injected directly into a graphite furnace. The use of iron(III) hexamethylenedithiocarbamate¹³ for cobalt determination and the use of iron(II) diethyldithiocarbamate¹⁴ and cobalt APDC¹⁵ for nickel determination require a long digestion of the precipitates to simplify the sample matrix.

This paper describes the fundamental conditions for the coprecipitation of trace amounts of cobalt and nickel in water with scandium hydroxide and for the determination of these ions by graphite-furnace atomic absorption spectrometry.

Experimental

Apparatus

A Hitachi 170-70 Zeeman atomic absorption spectrometer with a Hitachi cobalt or nickel hollow-cathode lamp was used for atomic absorption measurements. The optimum operating conditions, which were studied using a solution obtained by coprecipitation according to the recommended procedure from distilled water containing 100 ng of cobalt and nickel, are summarized in Table 1. For pH measurements, a Hitachi-Horiba Model M-5 glass-electrode pH meter was used.

Reagents

Cobalt and nickel solution. A solution containing about 1 mg cm⁻³ of cobalt or nickel was prepared by dissolving guaranteed reagent-grade metal nitrate in a small amount of concentrated

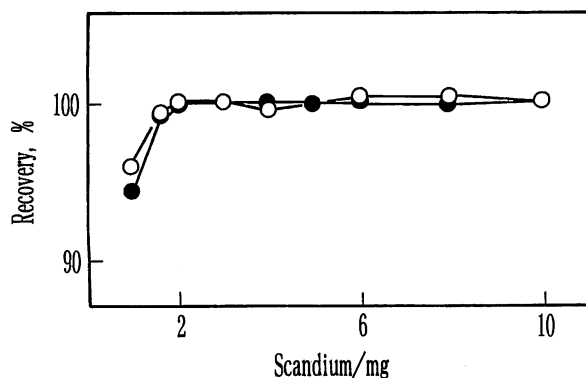


Fig. 1 Effect of the amount of scandium on the recovery of cobalt or nickel from 200 cm³ of a sample solution containing 1 µg of cobalt (○) or nickel (●). Coprecipitation was carried out at a pH of about 9.5, and the final sample volume was made up to 10 cm³.

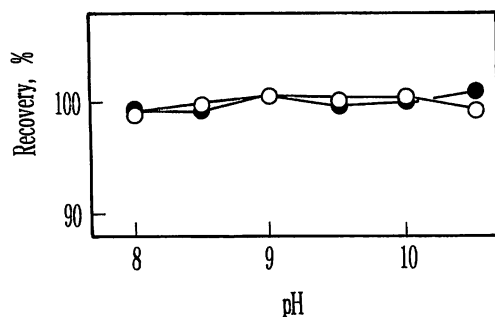


Fig. 2 Effect of the pH on the recovery of cobalt or nickel from 200 cm³ of sample solution containing 1 µg of cobalt (○) or nickel (●). Four milligrams of scandium were used for coprecipitation, and the final sample volume was made up to 10 cm³.

nitric acid and diluting with distilled water. The concentrations of both cobalt and nickel were determined by complexometric titration using Xylenol Orange and Murexide as indicators, respectively.

Scandium solution. About a 15 mg cm⁻³ scandium solution was prepared by dissolving scandium nitrate (Nacalai Tesque, Inc.) in distilled water. The scandium concentration was determined at a pH of about 2 by complexometric titration using Xylenol Orange as an indicator.

All other reagents used were of guaranteed reagent grade.

Recommended procedure

To a sample solution (up to 200 cm³) containing up to 100 ng of cobalt and 200 ng of nickel, 4 mg of scandium is added exactly, and the pH of the solution is adjusted to about 9.5 with a 0.1 mol dm⁻³ sodium hydroxide solution. To settle the produced precipitate, the solution is allowed to stand for a few minutes; the precipitate is then collected on a Toyo Roshi PTFE membrane filter (pore size 0.5 µm, diameter 25 mm), filtered by suction, washed with a small amount of distilled water, and dissolved with 0.5 cm³ of 1 mol dm⁻³ nitric acid. The atomic absorbances of cobalt and nickel were measured under the operating conditions given in Table 1. A blank using distilled water was run according to the same procedure as that for the sample solution. In this work the blank could be neglected in most instances because it was extremely small.

If it is difficult to make up the final volume to 0.5 cm³ with good reproducibility, the following measurement is

Table 1 Operating conditions for the atomic-absorption spectrometer

| | Co | Ni |
|-----------------------|--|--|
| Analytical wavelength | 241.6 nm | 232.0 nm |
| Lamp current | 7.5 mA | 10 mA |
| Slit width | No. 3 (2.2 nm) | No. 3 (2.2 nm) |
| Argon gas flow rate | | |
| Sheath gas | 3 dm ³ min ⁻¹ | 3 dm ³ min ⁻¹ |
| Carrier gas | 0 dm ³ min ⁻¹ | 0 dm ³ min ⁻¹ |
| Injection volume | 10 mm ³ | 10 mm ³ |
| Cuvette | Uncoated tube type graphite furnace | Uncoated tube type graphite furnace |
| Drying conditions | 24 A (ca. 190°C), 40 s | 24 A (ca. 190°C), 40 s |
| Ashing conditions | 80 A (ca. 900°C), 30 s | 80 A (ca. 900°C), 30 s |
| Atomizing conditions | 310 A (ca. 2830°C), 5 s | 310 A (ca. 2830°C), 5 s |

recommended: taking 10 mm³ of the final solution, the amount of cobalt or nickel in it (M_1 ng) is measured by graphite-furnace atomic absorption spectrometry under the operating conditions given in Table 1. Taking another portion of the solution (V mm³), the amount of scandium in it (S mg) is measured by complexometric titration using Xylenol Orange as an indicator. A blank is also run using distilled water as a sample solution. The content (M_0 ng) of cobalt or nickel in the original sample solution is calculated using the following equation:

$$M_0 = M_1 \times (V/10) \times (4/S).$$

Results and Discussion

Study of the optimum conditions for coprecipitation

Upon adding various amounts of scandium, its necessary amount for coprecipitation was examined with 200 cm³ of a sample solution spiked with 1 µg of cobalt or nickel. For the formation of scandium hydroxide, the pH of the sample solution was adjusted to about 9.5 with a 0.1 mol dm⁻³ sodium hydroxide solution. The precipitate produced was collected on a 3G4 sintered-glass filter, washed with a small amount of distilled water, and dissolved with 2 cm³ of 1 mol dm⁻³ of nitric acid. The solution was then made up to 10 cm³ with 1 mol dm⁻³ of nitric acid, and the absorbances of cobalt and nickel were measured under the operating conditions given in Table 1. From the results shown in Fig. 1, more than 2 mg of scandium was required for quantitative recoveries. The presence of up to 10 mg cm⁻³ of scandium did not affect the atomic absorption of cobalt or nickel. Thus, 4 mg of scandium was used in further experiments. The optimum pH range for the coprecipitation was 8.0 - 10.5 (Fig. 2). Therefore, the pH of the solution was adjusted to about 9.5 with a sodium hydroxide solution. The recoveries of cobalt and nickel were hardly influenced by the standing time of the precipitate. Thus, almost complete recoveries were obtained from a few minutes to 5 h of standing.

Dissolution of the precipitate

Scandium hydroxide dissolves easily in common mineral acids. The effect of the concentration of nitric and hydrochloric acids on the atomic absorbance of cobalt or nickel was examined. An increase in the concentration of these acids gradually decreased the absorbances. However, the absorbances of both metal ions became almost constant in the

Table 2 Effect of diverse ions on the determination of 50 ng of cobalt or nickel

| Mass ratio ^a [Ion]/[Co] or [Ni] | Ion |
|---|---|
| 1200000 | Na ⁺ |
| 500000 | K ⁺ |
| 250000 | Mg ²⁺ , Ca ²⁺ |
| 500 | Li ⁺ , Sr ²⁺ , Ba ²⁺ , Al ³⁺ , Ga ³⁺ , In ³⁺ , Sn ⁴⁺ , Pb ²⁺ , Sb ³⁺ , Bi ³⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺ , La ³⁺ , Ce ³⁺ , Zr ⁴⁺ , Mo ^{VI} , W ^{VI} , Cr ³⁺ , Mn ²⁺ , Fe ³⁺ , Pt ^{IV} , Au ^{III} |

The coprecipitation was carried out from about 50 cm³ of the sample solution at pH about 9.5.

a. The errors are within $\pm 5\%$.

Table 3 Recovery of cobalt and nickel from spiked water samples

| Sample volume/ cm ³ | Co | | | Ni | | |
|--------------------------------------|--------------|----------------|-----------|--------------|----------------|-----------|
| | Added/ ng | Recovery, % | RSD, % | Added/ ng | Recovery, % | RSD, % |
| River water | | | | | | |
| 200 | 5 | 98.8 | 8.7 | 10 | 97.3 | 7.5 |
| 200 | 50 | 99.6 | 5.3 | 100 | 100.5 | 5.7 |
| 200 | 100 | 99.2 | 4.0 | 200 | 100.1 | 5.8 |
| Seawater | | | | | | |
| 200 | 5 | 103.2 | 10.5 | 10 | 100.6 | 6.2 |
| 200 | 50 | 98.8 | 9.5 | 100 | 101.0 | 3.8 |
| 200 | 100 | 99.6 | 8.7 | 200 | 99.7 | 4.5 |

The recoveries were calculated by subtracting the peak height due to the water sample alone from one due to a water sample spiked with cobalt or nickel. The obtained recoveries are the average of three replicate determinations.

range of 0.4 – 2 mol dm⁻³ of nitric acid and 0.5 – 1.5 mol dm⁻³ of hydrochloric acid. In this study, 1 mol dm⁻³ of nitric acid was used for the dissolution of scandium hydroxide.

Calibration curves

Straight lines passing through the origin were obtained up to 100 ng of cobalt and 200 ng of nickel in the final solution using the recommended procedure. The relative standard deviations obtained from five repeated determinations were 4.7% and 5.7% for 50 ng of cobalt and nickel, respectively. The detection limits (signal/noise = 2) were 5.0 pg cm⁻³ of cobalt and 10.0 pg cm⁻³ of nickel in 200 cm³ of the initial sample solution.

Interferences

According to the recommended procedure, the effect of 27 foreign ions on the determination of 50 ng of cobalt or nickel was examined. Table 2 shows that large amounts of sodium, potassium, magnesium, and calcium did not interfere for both determinations. No other ions tested produced any serious interference effect, even at a concentration 500-times the mass of cobalt or nickel present.

Recoveries of cobalt and nickel from spiked water samples

The utility of the present method was evaluated by examining the recoveries of cobalt and nickel from river and seawater spiked with these metal ions. The obtained results are given in Table 3, indicating that the proposed method is applicable to

Table 4 Results of the determination of cobalt and nickel in water samples

| Location of sampling point | Calibration method | | Standard addition method | |
|-------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| | Co found/ ng cm ⁻³ | Ni found/ ng cm ⁻³ | Co found/ ng cm ⁻³ | Ni found/ ng cm ⁻³ |
| River (upper stream) | | | | |
| Asano | 0.050 | 0.27 | 0.049 | 0.26 |
| Sai | 0.034 | 0.066 | 0.038 | 0.068 |
| Kanakusari | 0.096 | 0.26 | 0.086 | 0.30 |
| Branch of | | | | |
| Gohtani | 4.15 ^a | 2.02 ^b | 4.22 ^a | 2.13 ^b |
| Seashore | | | | |
| Kanaiwa | N. D. | 0.23 | N. D. | 0.24 |

The sample volume taken was 200 cm³ and 0.5 cm³ of 1 mol dm⁻³ nitric acid was used for dissolution of the precipitate. The obtained results are the average of three replicate determinations. N. D.: not detected.

a. The final volume was made up to 10 cm³ with 1 mol dm⁻³ nitric acid.

b. The final volume was made up to 5 cm³ with 1 mol dm⁻³ nitric acid.

analyses of water samples containing down to 5 ng of cobalt and 10 ng of nickel in 200 cm³ of the initial sample solution.

Based on the above experiments, determinations of cobalt and nickel in river and seawater (located in Ishikawa prefecture) were tried. The samples were filtered through a Toyo Roshi TM-2p membrane filter (pore size 0.45 μ m) and analyzed as soon as possible after sampling. The results obtained by the calibration and standard addition methods were in good agreement, although cobalt in seawater was not detected (Table 4).

References

1. J. Ueda and T. Minami, *Chem. Lett.*, **1997**, 681.
2. S. Nakashima and M. Yagi, *Anal. Lett.*, **1984**, 17(A15), 1693.
3. M. Hiraide, Z. S. Chen, K. Sugimoto, and H. Kawaguchi, *Anal. Chim. Acta*, **1995**, 302, 103.
4. V. Hudnik, S. Gomiscek, and B. Gorenc, *Anal. Chim. Acta*, **1978**, 98, 39.
5. K. Cundeva and T. Stafilov, *Anal. Lett.*, **1997**, 30(4), 833.
6. M. Hiraide, Z. S. Chen, and H. Kawaguchi, *Anal. Sci.*, **1995**, 11, 333.
7. Z. S. Chen, M. Hiraide, and H. Kawaguchi, *Bunseki Kagaku*, **1993**, 42, 759.
8. Z. S. Chen, M. Hiraide, and H. Kawaguchi, *Mikrochim. Acta*, **1996**, 124, 27.
9. R. W. Dabeka, *Sci. Total Environ.*, **1989**, 89, 271.
10. K. Akatsuka, N. Nobuyama, and I. Atsuya, *Anal. Sci.*, **1989**, 5, 475.
11. Q. Zhang, H. Minami, S. Inoue, and I. Atsuya, *Anal. Chim. Acta*, **2000**, 407, 147.
12. M. Hiraide, Z. S. Chen, and H. Kawaguchi, *Talanta*, **1996**, 43, 1131.
13. K. Cundeva, T. Stafilov, and G. Pavlovska, *Microchem. J.*, **2000**, 65, 165.
14. H. Nishioka, S. Assadamongkol, Y. Maeda, and T. Azumi, *Nippon Kaisui Gakkaishi*, **1987**, 40, 286.
15. E. A. Boyle and J. M. Edmond, *Anal. Chim. Acta*, **1977**, 91, 189.