Introduction

Trace amounts of nickel at μg L⁻¹ levels must be determined using high-performance, expensive instrumentation, such as GFAAS, ICP-OES and ICP-MS, with typical detection limits for Ni of about 0.07, 0.5 and 0.0002 μg L⁻¹, respectively.¹ The cheaper and widely available FAAS method can be used if a preconcentration step is employed prior to analysis. Coprecipitation is a technique that is still in use today for the removal²,³ or preconcentration of metal ion.⁴,⁵ Thus, coprecipitation is one of the choices for nickel preconcentration in order to determine it at μg L⁻¹ levels by FAAS. Al(OH)₃ has been satisfactorily used as a coprecipitant of Cu, Cd and Pb from seawater and mineral-water samples to be determined by FAAS.⁶ To our knowledge, Al(OH)₃ has not been used before as a coprecipitant of Ni to be determined by FAAS.

Coprecipitation, nickel, aluminum hydroxide, preconcentration, flame atomic absorption spectrometry

Experimental

Nickel standard grade for AAS 1000 mg L⁻¹ was used. Analytical grades of Al(NO₃)₃·9H₂O, KCl, NaOH and HNO₃ were used.

A PinAAcle F900 Perkin Elmer FAAS was used with the 232.0 nm analytical line of Ni; slit width, 0.2 nm; hollow cathode lamp current, 25 mA; and 10 cm air-acetylene burner with an oxidizing flame. The nebulizer flow was 3.6 mL min⁻¹. A deuterium background correction was applied. A Sorvall LYNX 4000 centrifuge and a Mettler Toledo FiveEasy pH meter were used.

For Group III samples, the ASTM standard method of digestion¹⁰ was performed as follows: 500 mL of the sample was digested with 25 mL of 16 mol L⁻¹ HNO₃ on a hot plate until the volume decreased to 250 – 300 mL. The digested solution was cooled to room temperature and filtered, and then made up to a volume of 500 mL.

Notes

Determinación de Ni por espectrometría de absorción atómica de llama después de preconcentración por coprecipitación con hidróxido de aluminio

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A method for nickel preconcentration by coprecipitation using Al(OH)₃, followed by centrifugation and dissolution with HNO₃ prior to a determination by flame atomic absorption spectrometry (FAAS), was investigated. Preconcentration factors of 30 and 200 were tested, and the detection limit (3 × sd/m, n = 10) was 0.05 μg L⁻¹. The method was applied to real samples, and the results agreed with those obtained directly by graphite furnace atomic absorption spectrophotometry.

Keywords Coprecipitation, nickel, aluminum hydroxide, preconcentration, flame atomic absorption spectrometry

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Results and Discussion

Coprecipitation procedure for nickel determination

The detection limit of Ni by direct FAAS was determined on a blank solution (0.5 mL of 20% (v/v) HNO₃ and 20 μL of 10% (w/v) KCl in 2 mL) without Al(OH)₃ precipitation. The detection limit was 10 μg L⁻¹ Ni (3 ± sd/m where sd is the standard deviation of the blank signal for 10 replicates and m is the slope of the calibration curve given below). Consequently, 10 μg L⁻¹ Ni was initially used in testing the coprecipitation procedure. The calibration curve obtained for Ni²⁺ solutions without coprecipitation, y = 0.1178x + 0.00122, where y is the absorbance and x is the concentration (R² = 0.9990), was used to determine the concentration of Ni after coprecipitation. The concentrations obtained from the standard curve were divided by the PF to obtain the concentrations of Ni in the samples before coprecipitation.

Effect of pH on the coprecipitation procedure

The precipitation of 0.015 mol L⁻¹ Al(OH)₃ should occur at pH 3.4 (Kₚ Al(OH)₂ = 3 × 10⁻¹⁵). Thus, 60 mL of 10 μg L⁻¹ Ni was coprecipitated between pH 5 - 12 using 1 mol L⁻¹ NaOH delivered by a peristaltic pump. After centrifuging the Al(OH)₃ and coprecipitated Ni settled as a gelatinous layer.

The effect of pH on the recovery of Ni at a PF of 30 is shown in Fig. 1. Only a small amount of Al(OH)₃ precipitate was observed at pH 5, resulting in a negligible recovery (0.8%). The recoveries increased to a maximum when the pH increased from 6 to about 9 or 10 and then decreased sharply above pH 10. This decrease would be due to the dissolution of Al(OH)₃, as the aluminon ion [Al(OH)₃]⁻ forms. pH 10 was selected as the pH for Ni²⁺ coprecipitation in subsequent experiments.

Various concentrations of NaOH (0.5 - 4 mol L⁻¹) and addition flow rates (0.1 - 1.5 mL min⁻¹) were tested, but the recoveries were quite similar. As a compromise between the ease of pH adjustment and the time of the addition of 1 mol L⁻¹ NaOH delivered at 1 mL min⁻¹ at the beginning until pH 8, and then continued at 0.1 mL min⁻¹ to pH 10, were used in the majority of the experiments. The total time used for the addition of NaOH was about 5 - 7 min. When larger volumes of the sample and NaOH were used to give a PF of 200, 1 mol L⁻¹ NaOH was delivered at 4 mL min⁻¹ at the beginning until pH 8, and continued at 0.1 mL min⁻¹ to pH 10. Similar recoveries were obtained for standing times of 0, 15, 30, 45 and 60 min, indicating that the Ni coprecipitation was completed during the pH adjusting step, and a standing time is not needed in this work.

Effect of the amount of Al used for coprecipitation

It is important that enough Al be added to scavenge all of the Ni²⁺ present in solution by the Al(OH)₃ precipitate. In this work 4.9, 9.7, 14.6, 19.4, 24.3 and 29.2 mg of Al³⁺ were tested for the coprecipitation of 10 μg L⁻¹ (0.6 μg in 60 mL) and 50 μg L⁻¹ (3.0 μg in 60 mL) of Ni²⁺ at a PF of 30. The percent Ni²⁺ recoveries (%RNi²⁺) for 10 and 50 μg L⁻¹ of Ni²⁺ are plotted versus the mole ratio of Al:Ni in Fig. 2. In each series of experiments at constant [Ni²⁺], it is probable that the mole ratio of Al:Ni is the dominant variable. The two sets of data almost align (Fig. 2), and indicate that a good recovery is achieved when the mole ratio of Al:Ni >1.8 × 10⁴. At the 1.8 × 10⁴ mole ratio, the %RNi²⁺ was 100 ± 0.8 and 98 ± 1.4 for 50 μg L⁻¹ (3.0 μg) and 10 μg L⁻¹ (0.6 μg) of Ni²⁺, respectively; 4.9 mg of Al was used to coprecipitate 0.6 μg Ni at this ratio. When the same amount of Al (4.9 mg) was used to coprecipitate 3.0 μg Ni, the %RNi²⁺ was quite low (75 ± 2.4), because the Al:Ni mole ratio was only 3.6 × 10³. Originally, 24.3 mg of Al was used to coprecipitate 3.0 μg Ni at a 1.8 × 10⁴ mole ratio. When the same amount of Al (24.3 mg) was used to coprecipitate 0.6 μg Ni, the %RNi²⁺ was 100 ± 0.7 because the Al:Ni mole ratio was equal to 8.8 × 10⁴, much greater than the suggested threshold mole ratio of 1.8 × 10⁴. Therefore, 24.3 mg of Al was selected for coprecipitation in further work.

For lower concentrations of Ni²⁺, higher PF levels are required. Thus, a series of experiments were performed with Ni concentrations of 0.2 and 1 μg L⁻¹ with a PF of 200. Thus, the 400 mL of sample used contained 0.08 and 0.4 μg of Ni²⁺, respectively. The amount of Al was increased in the range 21.6 to 108 mg. From 24.3 mg of Al, 100% recovery was obtained, but below that level %RNi²⁺ began to decrease, even though the Al:Ni ratio was much greater than the threshold suggested above. The larger amounts of Al resulted in larger amounts of Al(OH)₃ precipitate, which is difficult to dissolve in 2 mL HNO₃, and the results became less reproducible. The findings suggest that 24.3 mg Al is suitable for the coprecipitation of Ni between 0.2 - 50 μg L⁻¹ with PFs between 30 - 200. However, the results do indicate that factors other than the PF are involved in determining %RNi²⁺ and a single criteria cannot be used for all conditions.

Method performance

The LOD and LOQ for a blank solution without preconcentration measured by FAAS was estimated to be 10 and 33 μg L⁻¹, respectively. The highest PF used in this work was 200. Therefore, the LOD and LOQ values with preconcentration are obtained by dividing these values by 200, giving a LOD of 0.05 μg L⁻¹ and a LOQ of 0.17 μg L⁻¹. Validation of the...
precision was performed in terms of the repeatability of 0.2 and 10 μg L⁻¹ Ni standard solutions. The relative standard deviations were 2.3 and 0.8% for the 0.2 and 10 μg L⁻¹ solutions, respectively (n = 3).

The method was applied to determine Ni in the prepared samples (Table 1). Firstly, the samples were determined directly by FAAS without preconcentration. The samples where Ni was not detected were then analyzed with coprecipitation preconcentration with a PF of 30.

The accuracy was evaluated by comparing this preconcentration FAAS method with direct GFAAS analysis (Table 1). From the analysis of a paired t-test, the t-stat value was 1.7 and the t-critical value was 2.8. Since t-stat < t-critical, the overall results for the two analyses were not significantly different at the 95% confidence level. However, in one sample (Spoon B vinegar) there is a significant difference between the FAAS method and the GFAAS method.

The results of Ni extracted by vinegar from stainless-steel spoons suggested that the lower priced spoon (A) can be corroded in acidic solutions, like vinegar. Therefore, leaving low quality spoons in condiments such as chilies pickled in vinegar should be avoided to prevent the uptake of Ni by consumers.

### Conclusions

A method for the determination of nickel by FAAS after preconcentration by coprecipitation with Al(OH)₃ was developed, tested and validated. The detection limit of nickel obtained was 0.05 μg L⁻¹ with a PF of 200 compared to 10 μg L⁻¹ for direct FAAS analysis. The method was applied to determine nickel in real samples with nickel concentrations below 10 μg L⁻¹ levels. The results from this method and GFAAS were not significantly different at the 95% confidence interval. Thus, the proposed method is a convenient and low cost alternative to methods like GFAAS, ICP-OES and ICP-MS.

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### References