Determination of Trace Amounts of Indium by Graphite-Furnace Atomic Absorption Spectrometry after Preconcentration as the Acetylacetonato Complex on Activated Carbon

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A rapid and simple preconcentration method by selective adsorption using activated carbon as an adsorbent and acetylacetone as a complexing agent is described for the determination of trace amounts of indium by graphite-furnace atomic absorption spectrometry. The indium-acetylacetonato complex is easily adsorbed onto activated carbon at pH 6.0 – 8.0. After the activated carbon phase, the adsorbing indium-acetylacetonato complex is separated and dispersed in 5 ml of a 2%(v/v) glycerine solution containing 700 µg of palladium. The resulting suspension of activated carbon is introduced directly into the graphite-furnace atomizer. The detection limit was 0.025 µg/1 (s/n=3), and the relative standard deviation was 4.0 – 5.0% at 1.0 µgIn/100 ml (n=10). This method was applied to the determination of indium in water samples and proved to be a useful technique for the preconcentration of trace amounts of indium in water samples.

Keywords Graphite-furnace atomic absorption spectrometry, indium-acetylacetonato complex, activated carbon, indium preconcentration

Indium is widely distributed in the crust of earth (as rocks and environmental samples) at a very low concentration level. It is therefore important to develop a method for the separation and preconcentration of trace amounts of indium. Although the separation of indium by ion-exchange or coprecipitation has been reported1-3, such procedures are time-consuming. Akama et al. researched the determination of trace amounts of indium by atomic absorption spectrometry after extraction with organic solvents.4,5 In recent years, methods for the adsorption of metals on activated carbon (AC) in the presence of chelating agents have been reported.6-12 Kimura et al. reported the separation and preconcentration of trace amounts of indium with AC used as an adsorbent.13 In the meantime, we have used AC in order to selectively separate and concentrate trace amounts of metal ions.14,15 Further, one of the present authors reported a method in which the AC-suspension adsorbing selenium—3-phenyl-5-mercapto-1,3,4-thiadiazole-2-thione complex16 and beryllium-acetylacetonato complex17 were directly introduced into the graphite furnace atomizer. These methods are very simple and suitable for determination after preconcentrating trace amounts of metals.

The ligand acetylacetone (acac) reacts with many metals to form metal-acac complexes, and has been extensively used as an extracting reagent of some metals. This paper describes a determination method of trace amounts of indium and its application. Namely, after trace amounts of indium are adsorbed onto AC as an acetylacetonato complex, the AC is separated from the mother liquid and is then dispersed in a definite volume of glycerine solution. The resulting AC-suspension is directly introduced into the graphite-furnace atomizer. The proposed method is simple and precise, and has proved to be useful for the determination of ppt levels of indium in water samples.

Experimental

Apparatus

Atomic absorption measurements of indium at the resonance line of 303.9 nm were carried out using a Shimadzu Model AA-680G atomic absorption spectrometer equipped with a deuterium background corrector, a GFA-4B graphite-furnace atomizer and a PK-5 graphic printer. A hollow-cathode lamp of indium was operated at 7 mA. Measurements of the concentration of indium were made in the peak-area mode. The optimal operating conditions for the GF-AAS are given in Table 1.

Reagents

A standard indium solution was prepared by consecutive dilution of 1000 µg/ml atomic absorption...
standard (Wako Pure Chemical Co. Ltd.) with 0.1 M HNO₃. Suprapure acetylacetone (Wako Pure Chem.) was used. Activated carbon (Merck No. 2186, smaller than 300 Tyler mesh) was used after purification with acid. The palladium used was of atomic absorption standard (Wako Pure Chem.). All of the other reagents used were of analytical reagent grade.

**Analytical procedure**

Three milliliters of 3%(v/v) acac solution was added to 100 - 1000 ml of sample solution containing less than 1.0 µg of indium and the pH was adjusted about 6.0 - 8.0 with diluted ammonia water. After 0.5 ml of the buffer solution (pH=7.0) and 60 mg of AC was added, the mixture was mixed for 15 min with an electromagnetical mixer. The indium-acac complex which was adsorbed quantitatively on AC was separated from the matrix solution through a membrane filter (pore size 8 µm). The AC adsorbed indium-acac complex was dispersed in 5 ml of 2%(v/v) glycerine solution containing 700 µg palladium for 20 s with an ultrasonic agitator. After shaking for 15 s, a 10 µl aliquot of the AC-suspension was directly injected into a graphite furnace with an Eppendorf micropipet. The peak-area was measured under the conditions given in Table 1.

**Results and Discussion**

**Matrix modifier**

Indium, being a volatile element, has been known to be one of the difficult elements to determine by GF-AAS. Therefore, GF-AAS using palladium, lanthanum and nickel etc. as a matrix modifier for the determination of indium was reported. The palladium-indium compound which was adsorbed quantitatively on AC was separated from the matrix solution through a membrane filter (pore size 8 µm). The AC adsorbed indium-acac complex was dispersed in 5 ml of 2%(v/v) glycerine solution containing 700 µg palladium for 20 s with an ultrasonic agitator. After shaking for 15 s, a 10 µl aliquot of the AC-suspension was directly injected into a graphite furnace with an Eppendorf micropipet. The peak-area was measured under the conditions given in Table 1.

**Effect of the pH on the adsorption of an In acac complex**

The effect of the pH on the adsorption of indium onto AC was examined with the proposed procedure. The result is shown in Fig. 2. The main effect of a modifier may be ascribed to the formation of a relatively non-volatile palladium-indium compound in the graphite tube. AC is not only used for the adsorption and collection of indium, but also plays the role of a modifier. Therefore, in the proposed procedure, AC was used as an adsorbent for the preconcentration of trace indium. Further, glycerine was added to the suspension in order to make it suitable as a dispersent of AC.

**Effect of the temperature of atomization**

The effect of the temperature of atomization on the adsorption of indium onto AC was examined with the proposed procedure. The result is shown in Fig. 1. The main effect of a modifier may be ascribed to the formation of a relatively non-volatile palladium-indium compound in the graphite tube.

<table>
<thead>
<tr>
<th>Operating step</th>
<th>Temperature/°C</th>
<th>Time/s</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>120</td>
<td>10</td>
<td>ramp</td>
</tr>
<tr>
<td>Ashing</td>
<td>800</td>
<td>30</td>
<td>ramp</td>
</tr>
<tr>
<td>Atomization</td>
<td>2500</td>
<td>3</td>
<td>step</td>
</tr>
</tbody>
</table>

Wavelength, 303.9 nm; lamp current, 7 mA; Ar gas flow rate, 1.51 min⁻¹.
Effects of the amounts of activated carbon and acetylacetone

The effects of the amount of AC and acac on the adsorption of indium-acac complex at pH 7.0 were examined (Fig. 3). Quantitative adsorption of indium was obtained at more than 55 mg of AC and 3 ml of 5%(v/v) acac. Then, when more than 70 mg of AC was employed for the analytical procedure, AC was not well dispersed into water, and it was difficult to exactly take a definite amount of the AC-suspension. Accordingly, in this work, 60 mg of AC was used for the determination of indium. Moreover, the indium-acac complex was quantitatively adsorbed onto AC by mixing for about 10 min.

Calibration graph and detection limit

The influence of the sample size was investigated by varying the volume of a sample containing 0.2 µg or 1.0 µg of indium, respectively. The recoveries of indium obtained with the proposed procedure were all over 98% in the 100 – 1000 ml range. Thus, the use of a 1000 ml sample aliquot can give a concentration factor of 200.

The calibration graph obtained with the proposed analytical procedure for a 100 ml sample aliquot was linear up to 1.0 µg indium. The detection limit of indium was 0.025 µg/1(S/N=3) and the relative standard deviation of ten measurements was 4.0 – 5.0% at 1.0 µgIn/100 ml.

Adsorption isotherms

Freundlich's adsorption isotherms are generally applicable for the monomolecule adsorption of a single species from the liquid to solid phase. The equation can be expressed as

\[ q = kC^{1/n} \]

and

\[ \log q = \log K + \frac{1}{n} \log C \]

where \( q \) is the adsorption amount (g g\(^{-1}\)), \( C \) is the residual amount (g ml\(^{-1}\)) and \( K \) and \( 1/n \) are arbitrary parameters. Under the above conditions, Freundlich's adsorption isotherms were drawn; the results are shown in Fig. 4.

At first, the procedure was carried out for a system without acac (□). The procedure was repeated in the presence of acac (○). Indium could not be selectively and quantitatively adsorbed onto AC in the presence of AC alone. On the other hand, the proposed method is better regarding into adsorption ability.

Table 2 summarizes the isotherm parameters. The value of \( 1/n \) is usually less than 1. When the value is greater than 2, adsorption is difficult. The values for the two methods were less than 1, respectively. Consequently, both the proposed method and employing only AC result in good adsorption.

Moreover, the adsorption ability is also higher when the value of \( k \) is large. Therefore, the proposed method using the indium-acac complex is effective for the preconcentration of trace amounts of indium.

Effect of diverse ions

The effect of foreign ions included in natural and seawater samples was examined against a 100 ml sample involving 1.0 µg of indium and coexisting respective ions. The experimental results are given in Table 3. These results show that a number of common ions do not interfere with the determination of indium.

Although minute amounts of Fe\(^{III}\) interfere with the determination of indium by the proposed procedure, this problem was solved by adding sodium fluoride as a masking agent. Then, calcium(II) and magnesium(II)
ions gave a fairly large interference. Although various techniques to mask these ions were attempted for the determination of indium in seawater, satisfactory results could not be obtained. Therefore, the proposed method cannot be applied to the determination of indium in seawater samples. However, many ions were tolerated at the concentrations present in natural water samples, except for seawater.

**Application**

The indium contents in both spring and well water were determined by the proposed method. After suspended matter was removed using a membrane filter (pore size 0.45 µm), a 100 or 500 ml sample aliquot was employed for the determination of indium according to the analytical procedures. The obtained results are given in Table 4. Indium in the sample solutions employed could not be determined when less than the detection limit (0.025 ppb) was present. To evaluate the effect of matrix detection in the water, after samples containing a known amount of indium were added to each sample analyses were carried out. Quantitative recoveries were also obtained for each sample.

In summary, the proposed method is a simple, rapid and reliable technique for the preconcentration of trace amounts of indium in water samples.

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**References**


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