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RECOMBINATION REACTION BETWEEN INDIUM AND CHLORINE IN AIR-ACETYLENE FLAME OBSERVED BY MOLECULAR FLAME ABSORPTION SPECTROSCOPY

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When a solution of indium dissolved in $HClO_4$ was aspirated into an air-acetylene flame, molecular absorption spectrum of InCl in the flame was observed by molecular flame absorption spectroscopy. This indicates that the recombination reaction between indium and chlorine occurs in the flame, following the thermal decomposition of $HClO_4$.

Molecular absorption spectroscopy in flame has been developed and reported in our previous papers(1-4). Molecular absorption spectrum of SO_2 was observed in an air-hydrogen flame, utilizing the 273 cm long tube burner, and sulfur in biological samples was analyzed at 207 nm(1). When phosphoric acid in an aqueous solution was aspirated into an air-acetylene or a nitrous oxide-acetylene flame, a diatomic molecule of PO is produced in the flames, and it gives absorption bands near 246 nm(2,3). Moreover, it has been shown that the absorption band at 246.0 nm can be applied to the direct determination of phosphorus in nucleotides(2). When indium ion in HCl aqueous solution was aspirated into the air-acetylene flame, molecular absorption spectrum of InCl was observed near 267 nm(4). The formation of InCl in the flame clearly explains the chemical interfering effect of HCl in indium atomic absorption spectrometry(4,5). Thus, the study of the molecular absorption spectra in flame is useful for both the analysis of the non-metallic elements and the investigation of the chemical interfering effects in atomic absorption spectrometry besides the fundamental interest in the species appeared and their spectra. In the present paper, molecular absorption spectroscopy has been used to elucidate the formation mechanism of InCl, aspirating a solution of indium in $HClO_4$ into the air-acetylene flame.

For the measurements of atomic and molecular absorptions, HITACHI 207 Atomic Absorption Spectrophotometer was used without any modification. The burner used was the 10 cm slot one for atomic absorption spectrometry. In the case of the measurement of the molecular absorptions, a deuterium lamp of the hollow cathode type was used as a light source, which was obtained from HAMAMATSU TV Co. The molecular absorption spectrum of InCl shown in Figure 1 was obtained by measuring the absorbances at wavelengths with the interval of 0.1 or 0.2 nm. Atomic absorption of indium in the air-acetylene flame was measured at 303.9 nm by using an indium hollow cathode lamp, which was obtained from Westinghouse Co. Ltd. The sample solutions were prepared by dissolving In_2O_3 into acidic aqueous solutions. In_2O_3(99.9 %) was obtained from MITSUWA Chemical Ind. Co.

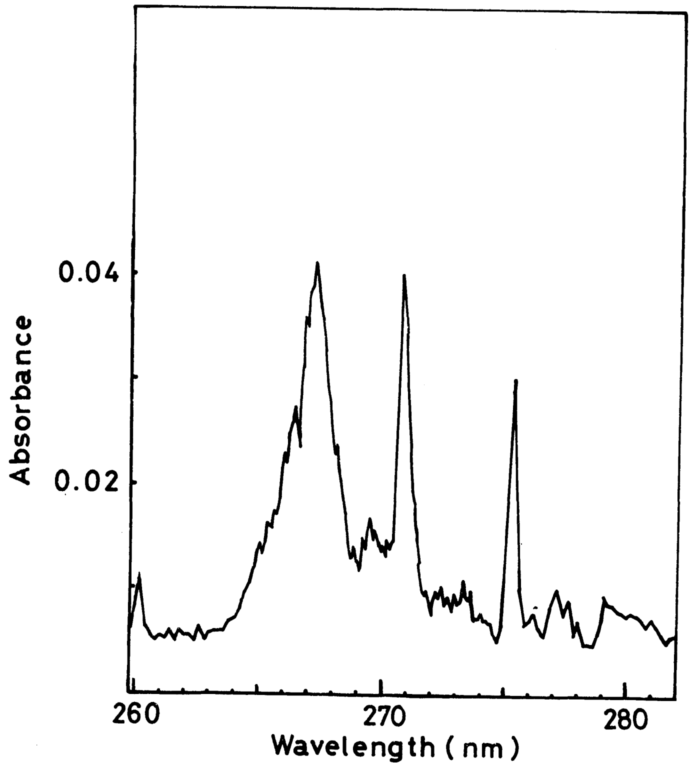


Figure 1. Atomic and molecular absorption spectrum of indium in the presence of $HClO_4$ in air-acetylene flame. (Concentration of indium: 0.05 M, Concentration of $HClO_4$: 2 N, Air flow rate: 13 l/min, Acetylene flow rate: 3 l/min, Flame height: 1 cm, Lamp current: 30 mA)

Molecular absorption spectrum observed when an aqueous solution of 0.05 M indium in 2 N $HClO_4$ was aspirated into the air-acetylene flame is shown in Figure 1. In the spectrum, the sharp lines at 260.1, 271.4, 275.2 and 277.5 nm are due to the atomic absorption of indium, In I, and the absorption band near 273 nm the molecular absorption of InO, as has been reported in the previous paper(4). In the spectrum shown in Figure1, the absorption bands at 266.1, 267.2, 268.4, 269.5, 271.8 and 274.1 nm are also observed. These bands are consistent with those of InCl, which are observed when indium ion in HCl aqueous solution is aspirated into the air-acetylene flame(4). It has been known that these absorption bands consist of two series of the vibrational systems(6); λλ 267.2 nm(0 - 0), 269.5 nm(0 - 1), 271.8 nm(0 - 2), 274.1 nm(0 - 3), and λλ 266.1 nm(1 - 0), 268.4 nm(1 - 1). From the fact mentioned above, it can be concluded that InCl is produced in the flame when indium ion in $HClO_4$ is aspirated into the air-acetylene flame. Since an indium ion does not directly bind to a chlorine atom in $HClO_4$ solution, the above result suggests that chlorine atom is produced in the flame according to the pyrolysis of perchloric acid. A sequence of reactions such as the following may occur in the flame;

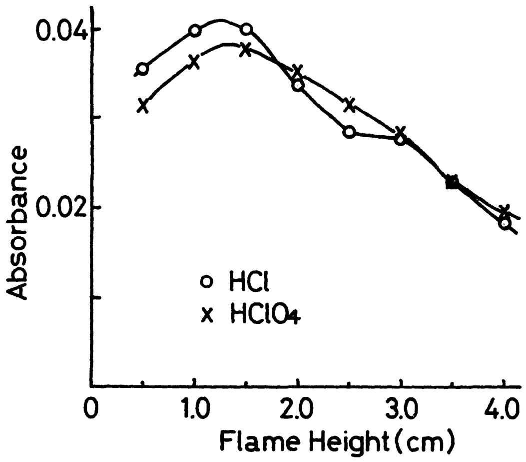
$$HClO_4 \xrightarrow{\Delta} \frac{1}{2}H_2O + \frac{3}{2}O_2 + \underline{Cl} \qquad (1)$$

$$In(ClO_4)_3 \xrightarrow{\Delta} \underline{In} + 3\underline{Cl} + 6O_2 \qquad (2)$$

$$\underline{In} + \underline{Cl} \longrightarrow InCl \qquad (3)$$

where Δ shows a pyrolysis reaction, and the overall chemical equivalents were neglected. Reaction 3 indicates that chlorine and indium atoms, which are produced by the pyrolysis reactions of $HClO_4$ and $In(ClO_4)_3$ expressed by Reactions 1 and 2, res-

Figure 2. Dependence of absorbance of InCl at 267.2 nm on the flame height over the burner in the air-acetylene flame, when aqueous solutions of 0.05 M indium one in 2 N HCl and the other in 2 N $HClO_4$ were aspirated into the flame.(Air flow rate: 13 l/min, Acetylene flow rate: 3 l/min, Lamp current: 30 mA)



pectively, recombine each other in the flame. Such a recombination reaction is supported by the following experimental result shown in Figure 2. In Figure 2, the dependence of the absorbance of InCl on the flame height over the burner in the air-acetylene flame was measured when the solutions of 0.05 M indium in both 2 N HCl and $HClO_4$ were aspirated into the flame. As can be seen from Figure 2, the absorbance of InCl in the presence of HCl is larger than that in $HClO_4$ at the lower flame position, and such a relation reverses at the flame position over 2 cm. This fact may clearly indicate that the formation reaction rate of InCl is less in the $HClO_4$ solution than in HCl solution. This may be due to the different formation mechanisms of InCl in the two solutions. That is, in the perchloric acid solution, InCl is formed by the recombination reaction(Reaction 3) right after the successive pyrolysis(Reactions 1 and 2), whereas in the hydrochloric acid solution it is directly produced by the dehydration and the pyrolysis of indium chloride compounds, as shown in Reaction 4;

$$\underbrace{InCl_x(H_2O)_{6-x}^{3-x}}_{\text{in solution(7)}} \xrightarrow{\text{dehydration}} \underbrace{(In\text{-}Cl)Cl_2 \xrightarrow{\text{pyrolysis}} InCl}_{\text{in flame}} \qquad (4)$$

where In-Cl represents the coordination bond between In and Cl. Reaction 4 must be much faster than the series of Reactions from 1 to 3. The similar formation of the intermediate compound between metal and the coordination atoms has been observed in the case of cobalt atomic absorption spectrometry for cobalt(III) complexes(8).

The formation of InCl in the air-acetylene flame explains, in addition, clearly the chemical interfering effect of $HClO_4$ in indium atomic absorption spectrometry. The dependence of indium atomic absorption on the concentration of $HClO_4$ in the air-acetylene flame, which was observed at 303.9 nm in this work utilizing HITACHI 207

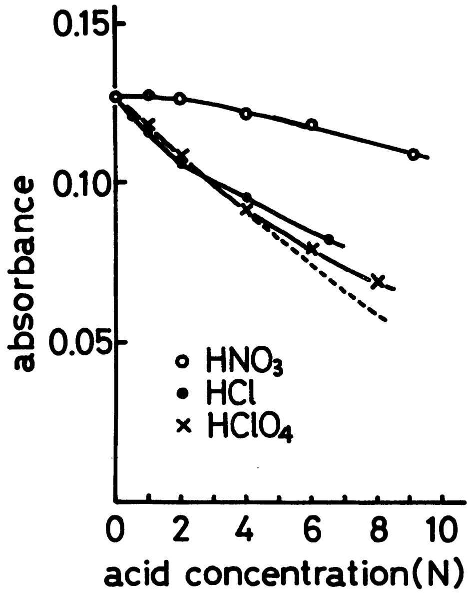


Figure 3. Chemical interfering effect of $HClO_4$ on indium determination by atomic absorption measured at 303.9 nm in the air-acetylene flame; Tha dotted line shows the observed absorbances for $HClO_4$ solutions.(Concentration of indium: 20 μg/ml, Air flow rate: 13 l/min, Acetylene flow rate: 3 l/min, Flame height: 1 cm, Lamp current for an indium hollow cathode tube: 15 mA)

Atomic Absorption Spectrometer and an indium hollow cathode lamp, are shown in Figure 3, along with the results in the cases of HNO_3 and HCl. In Figure 3, the dotted and the continuous lines for the case of $HClO_4$ imply the observed and the corrected results, respectively. The absorbance of indium was corrected because of the change of the flow rate of the sample solutions into the flame due to the increase of acid concentration. The method of such a correction is the same reported by Takada and Nakano(9). In the cases of HNO_3 and HCl solutions, the corrections were negligible. It can be seen from Figure 3 that $HClO_4$ interferes with the indium atomic absorption as HCl does. The mechanism of the chemical interfering effect can be understood by the formation of InCl in both cases, as is mentioned above.

The molecular absorption band of InCl has the possibilities of the application to the analysis of chlorine by flame spectrometry. Such an application is in progress.

REFERENCE

1. K. Fuwa and B. L. Vallee, Anal. Chem., 41, 188 (1969).
2. K. Fuwa, H. Haraguchi, K. Okamoto and T. Nagata, Japan Analyst, 21, 945 (1972).
3. K. Fuwa, H. Haraguchi and S. Toda, International Congress on Analytical Chemistry, Kyoto, April 3-7, 1972.
4. H. Haraguchi and K. Fuwa, Chemistry Letters, 1972, 913.
5. P. E. Popham and W. G. Schrenk, Spectrochim. Acta, 24B, 223 (1969).
6. R. W. B. Pearce and A. G. Gaydon, "The Identification of Molecular Spectra" (1950), Chapman and Hall Ltd., London.
7. H. Haraguchi, K. Fuwa and S. Fujiwara, J. Phys. Chem., in press.
8. K. Fujiwara, H. Haraguchi and K. Fuwa, Anal. Chem., 44, 1895 (1972).
9. T. Takada and K. Nakano, J. Chem. Soc. Japan, 90, 279 (1969).

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