The Application of Molecular-flame-absorption Spectroscopy to the Elucidation of Chemical Interferences in Indium Atomic Absorption Spectrometry

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The atomic absorption spectrometry of indium was investigated in air-acetylene and nitrous oxide-acetylene flames. The atomic absorptions of indium were significantly interfered by HCl, $HClO_4$, and HBr in both the flames. The chemical interferences can be explained by the formation of diatomic molecules, such as InCl and InBr, the molecular absorption spectra of which were really observed in flames.

The atomic absorption spectrometry of indium has been studied by several workers.[1-4] It has been established by the studies that indium is interfered with by several cations[2] and anions[4] in the air-acetylene flame and even in the nitrous oxide-acetylene flame. Popham and Schrenk reported analytical interferences by HCl, HBr, H_2SO_4, and H_3PO_4 in the concentration range of less than 1M and suggested an interfering mechanism resulting from the formation of diatomic molecules in the flames.[4]

Recently, the molecular absorption spectra of various species in flames have been investigated, and such molecular species as SO_2, PO, InF, InCl, InBr, InO, AlF, AlCl, and AlO have been found.[5-11] Furthermore, it has been shown that these molecular absorption spectra in the flames can be used not only for the determination of non-metallic elements,[5-7] but also for the elucidation of the chemical interferences.[8,9] Hence, in this paper, the chemical interferences due to various hydrogen acids in indium atomic absorption spectrometry have been investigated by means of molecular absorption spectroscopy.

Experimental

Samples. The indium oxide (In_2O_3; 99.9%) was purchased from Mitsuwa Chemical Ind. Co. The acids used were of a guaranteed ragent grade. The sample solutions were prepared by dissolving properly weighed amounts of indium oxide in acidic aqueous solutions.

Instruments. A Hitachi 207 Atomic Absorption Spectrophotometer was used for the measurements of the atomic and molecular absorptions. The hollow cathode-discharge tube of indium was obtained from Hitachi Manufacturing Ltd., and that of the deuterium lamp, from the Hamamatsu TV Co. A Hitachi 207-0100 High-voltage Power Source was used as the power supply for the deuterium lamp.

Procedures. The experimental conditions for the measurements of the atomic and molecular absorptions in the air-acetylene and nitrous oxide-acetylene flames are summarized in Table 1. In the case of the atomic absorption spectrometry, the "sample flow rates," which are referred to the volumes of the sample solutions aspirated into the burner for a minute, are affected to some extent by the viscosities of the solutions and change the atomic absorptions of indium. Therefore, the dependences of the atomic absorptions on the sample-flow rates have been investigated. The results are shown in Fig. 1, where the sample flow rates were changed by using several kinds of capillary tubes with different diameters and lengths. The sample flow rates were measured with a graduated cylinder.

TABLE 1. EXPERIMENTAL CONDITIONS IN ATOMIC AND MOLECULAR ABSORPTION SPECTROMETRY

I) ATOMIC ABSORPTION	
Analytical lines	303.9 nm, 325.6 nm, 412.5 nm, 451.1 nm
Lamp	hollow cathode lamp of indium
Lamp current	15 mA
Flame height	10—20 mm
Air–acetylene flame;	
air flow rate	13 l/min
acetylene flow rate	3 l/min
Nitrous oxide–acetylene flame[a];	
nitrous oxide flow rate	6 l/min
acetylene flow rate	4 l/min
Spectral band width	0.34 nm
II) MOLECULAR ABSORPTION[b]	
Analytical lines	(303.9 nm for In) 273.0 nm for InO 267.2 nm for InCl 284.6 nm for InBr
Lamp	hollow cathode lamp of deuterium
Lamp current	25—35 mA

a) A water-cooled burner for nitrous oxide–acetylene flame was used. b) Other conditions were the same with those in atomic absorption spectrometry.

The molecular flame absorption spectrum shown in Fig. 5 was obtained by measureing the absorbances at wavelengths separated by intervals of 1Å, as has been reported previously,[11] the deutrium lamp was used as a continuous light source. The dependences of the atomic and molecular absorptions of In, InO, and InCl on the HCl concentration, which are shown in Fig. 4, were also measured using the deuterium lamp.

Results and Discussion

The calibration curve for the atomic absorption of indium was linear in the concentration range from 0 to 10 μg/ml when 0.1—1 M HNO_3 aqueous solutions of indium with various concentrations were used as the sample solutions. The sensitivity (1% absorption) for

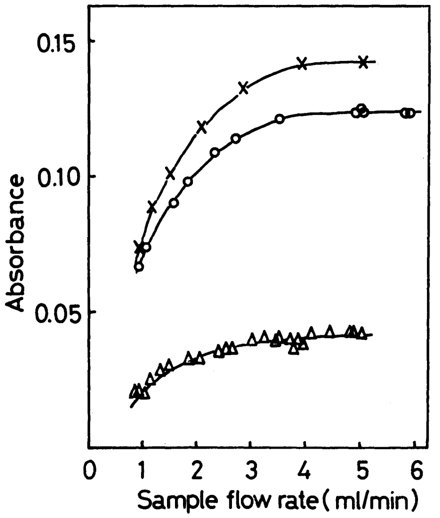

Fig. 1. Sample flow rate *vs.* atomic absorptions of indium at several analytical lines in the air–acetylene flame.

The concentration of indium is 20 µg/ml.
—×—: 303.9 nm, —○—: 325.6 nm
—△—: 412.5 nm, 451.1 nm.

the analytical lines of 303.9, 324.6, 410.5, and 451.1 nm were 0.5, 0.6, 1.7, and 1.7 µg/ml respectively.

Dependences of the Atomic Absorptions on the Sample-flow Rate. The atomic absorptions of indium are much affected by the sample-flow rates. The experimental curves for the relation between the absorbances of atomic indium in the air-acetylene flame and the sample-flow rates are shown in Fig. 1; these curves correspond to the results with respect to some analytical lines. In all the cases, the absorbances of indium significantly decrease when the sample-flow rates become smaller than 3.5 ml/min, while they are almost constant over 3.5 ml/min. Similar results have been obtained by Fuwa *et al.* in flame-emission spectrometry[12] and by Takada and Nakano in atomic absorption spectrometry.[13] In the emission spectrometry, the intensity is very dependent on the sample-flow rate, and the maximum intensity was observed clearly at a definite sample-flow rate.[12] These results have been explained in terms of the cooling effect of the aspirated water on the flame temperature. This is because the population of atoms in the exited states, which determines the sensitivity of emission, depends much on the flame temperature. In atomic absorption spectrometry, on the other hand, the population of atoms in the ground state determines the sensitivity; it dose not depend greatly on the change in the flame temperature.[13] Therefore, the results in Fig. 1 indicate that the changes in the sample-flow rates are not so meaningful in atomic absorption spectrometry as in emission spectrometry.

Interferences of Hydrogen Acids. The dependences of atomic absorptions in the air–acetylene flame on the concentration of hydrogen acids are shown in Fig. 2. When the concentrations of acids become larger, the viscosities of the sample solutions increase and the sample-flow rates decrease significantly, below 3.5 ml/min in some cases. Such effects of acids were particularly remarkable in the cases of H_2SO_4 and $HClO_4$. These circumstances are shown in Fig. 2, where the observed values have been corrected using the results shown in Fig. 1. In the cases of other acids, the effects of the viscosities of the solutions were smaller or negligible. From Fig. 3, it can be seen that the stomic absorptions of indium are considerably interfered with by various hydrogen acids as the acid concentrations increase. The interferences become larger in the following order; $HNO_3 < H_2SO_4 < HI < HBr < HClO_4 \cong HCl$. These interferences can not be excluded even in the nitrous oxide–acetylene flame, as is shown in Fig. 3. It should be noted here that indium in $HClO_4$ is interfered with to almost the same extent as that in HCl.

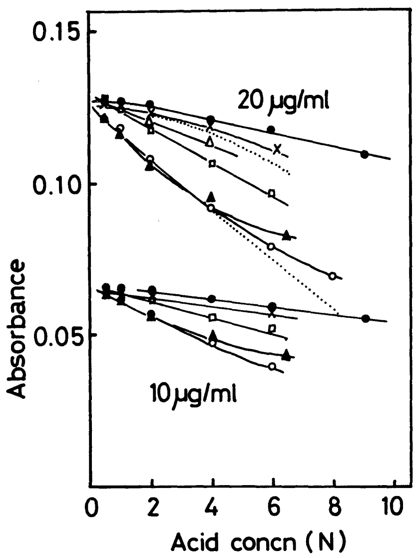

Fig. 2. Chemical interfering effects of hydrogen acids on atomic absorptions of indium at 303.9 nm in the air–acetylene flame.

The concentration of indium is 10 and 20 µg/ml. The dotted lines show the obserbed values in the cases of H_2SO_4 and $HClO_4$, and the continuous lines do the corrected values with respect to the viscosities of the sample solutions in the respective case.
—●—: HNO_3, —×—: H_2SO_4, —△—: HI,
—□—: HBr, —▲—: HCl, —○—: $HClO_4$.

Sastri *et al.* investigated the atomic absorptions of Ti, Zr, Ta, Hf, and so on in cyclopentadiene and acetylacetonate complexes, and suggested that the dissociations of metal complexes into atoms in the flame are controlled by the atoms directly coordinated with the central metal ion in ligands.[15,16] According to their investigation of the distributions of cobalt atoms in the flame, Fujiwara *et al.* also suggested the formation of intermediate molecules between the central metal ion and the coordinating atom in the case of cobalt(III) complexes.[17] Moreover, Popham and Schrenk explained the interferences of hydrogen acids less than 1 M with the atomic absorptions of indium by suggesting the formation in the flame of such intermediate compounds as InO and InCl.[4] Actually, Marks and Welcher observed the flame emissions of such diatomic molecules as AlO and TiO and interpreted the metallic inter-element interferences in aluminum atomic absorption spectrometry as occurring because of the reaction between the diatomic molecules.[18] The studies cited

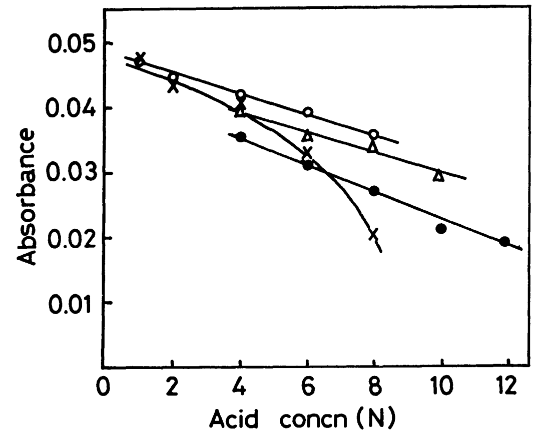

Fig. 3. Chemical interfering effects of hydrogen acids on atomic absorptions of indium at 303.9 nm in the nitrous oxide–acetylene flame.
The concentration of indium is 10 μg/ml.
—○—: HNO_3, —△—: HBr, —●—: HCl
—×—: $HClO_4$.

above suggest the important roles of the intermediate molecules, such as the diatomic molecules, in the chemical-interfering phenomena. With respect to the HCl and HBr solutions of indium, the molecular absorptions of InCl and InBr have been observed in the air–acetylene flame, when the solutions are aspirated into the flame.[8–11]

TABLE 2. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES OF INDIUM[21]

Molecule	Dissociation energy (eV)
InO	3.3 ±0.5
InI	3.35±0.15
InBr	4.0 ±0.15
InCl	4.5 ±0.15
InF	5.35±0.15
InH	2.5[a]

a) Cited from "Flame Spectroscopy" by R. Mavrodineanu and H. Boiteux, John Wiley & Sons, New York (1965).

It has been established by the ^{115}In-NMR study that indium ions in various hydrogen acids exist as such complexes as $In(H_2O)_6^{3+}$ in HNO_3 and $HClO_4$, $In(SO_4)_2^-$ in H_2SO_4, and $In(H_2O)_{6-n}X_n^{3-n}$ in HCl, HBr, and HI, where X is Cl, Br, and I and where n is 0—4.[19,20] If we take into consideration the suggestions with respect to the decompositions of various complexes in the flames, as proposed by Sastri *et al.*[15,16] and Fujiwara *et al.*,[17] it is possible that indium in various acidic solutions produces, in the flame, such diatomic molecules as InO, InS, InCl, InBr, and InI as intermediate compounds. If so, the interferences due to hydrogen acids may have some correlation with the dissociation energies of the suggested diatomic molecules. The dissociation energies of the diatomic molecules are listed in Table 2.[21] The order of magnitudes of the dissociation energies is really consistent with that of the interferences due to hydrogen acids except for the case of $HClO_4$. This may support the idea of the formation of diatomic molecules in the flame. Indium in the $HClO_4$ solution behaves similarly to that in HCl in both the air–acetylene and nitrous oxide–acetylene flames. This may be ascribed to the formation of InCl by a secondary reaction in the flame in the case of $HClO_4$. This interfering mechanism will be elucidated in the next section.

The reason why the interferences of acids cannot be overcome even in the nitrous oxide–acetylene flame may be ascribed to the fact that the dissociation energies of the diatomic molecules shown in Table 2 are large enough so that the diatomic molecules are dissociated into atoms only with difficulty, even in the nitrous oxide–acetylene flame.

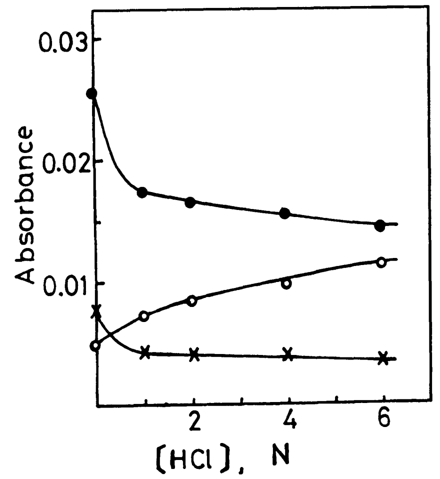

Fig. 4. Concentration of HCl *vs.* atomic and molecular absorptions of indium in the air–acetylene flame. The concentration of indium is 0.05 M, and a deuterium lamp was used.
—●—: In at 303.9 nm, —×—: InO at 273.0 nm,
—○—: InCl at 267.2 nm.

Interfering Mechanisms. In order to elucidate the interfering mechanisms suggested above, the atomic and molecular absorptions for the indium atoms, InO and InCl, in the air–acetylene flame were measured in terms of the HCl solution of indium, using a deuterium lamp. The results are shown in Fig. 4, where the concentration of indium was 0.05 M and where the analytical lines for In, InO, and InCl were 303.9 nm, 273.0 nm, and 267.2 nm[11] respectively. As the concentration of HCl increase, the absorbances of InCl increase, while those of In and InO decrease. This fact indicates that the interfering effect of HCl is apparently due to the formation of InCl in the flame. The increase of the interference at the high concentrations of HCl may also be affected by that of the complex formation of indium with chlorine in solution.[20] In the case of HBr, result similar to that in Fig. 4 was obtained, and it was ascertained that the formation of InBr is essential to the interfering effect of HBr.

In Fig. 5 the absorption spectrum is shown; it was measured by aspirating the $HClO_4$ solution of indium into the air–acetylene flame. It should be noted here that the broad bands observed in the range from 265 to

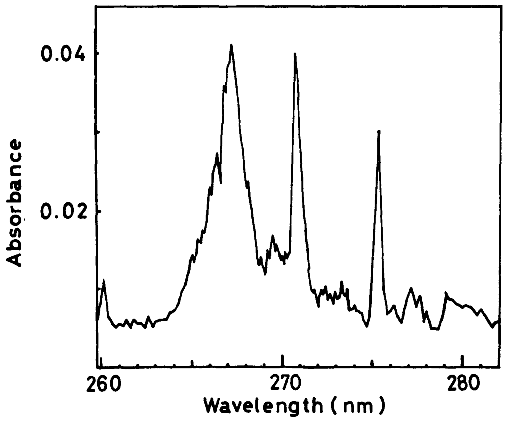

Fig. 5. Absorption spectrum in the airacetylene flame, which are measured with aspirating an 2 N $HClO_4$ solution of 0.05 M indium into the flame.

270 nm correspond to those of InCl.[11] This result indicates that the following reactions for the formation of InCl occur in the flame and that InCl is produced:

$$In(ClO_4)_3 \xrightarrow{\Delta} In^* + 3Cl^{**} + 6O_2$$
$$HClO_4 \xrightarrow{\Delta} Cl^{**} + OH + 3/2O_2$$
$$In^* + Cl^{**} \longrightarrow InCl$$

where Δ indicates a pyrolysis reaction. The formation of InCl in the case of the $HClO_4$ solution of indium explains well the results of atomic absorption spectrometry shown in Figs. 2 and 3.

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