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MOLECULAR ABSORPTION SPECTRUM OF InCl IN FLAME

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Molecular absorption spectrum of InCl was observed in the flame for the first time at the wavelengths near 2670 Å, when 0.2 M indium in 2 M HCl aqueous solution was aspirated into the air-acetylene flame. The absorption band of InO was, also, observed near 2730 Å in the same spectrum.

Atomic absorption spectrometry has been increasingly applied in the various fields. However, atomic absorption of non-metallic elements such as sulfur, phosphorus and halogens cannot be observed by the usual method using the flame because of their resonance lines existing in the far ultraviolet region. It has been known that the non-metallic elements give the molecular absorption bands in the regular ultraviolet or the visible region, when their compounds are excited in a high-frequency discharge tube or in flames(1). Therefore, if those molecular absorption bands could be observed in the flame, quantitative analysis of non-metallic elements would be possible by the usual flame method like atomic absorption spectrometry. As for sulfur and phosphorus, we previously showed that the determinations of these elements can be carried out by utilizing the absorption bands of SO_2 near 2070 Å(2) and of PO near 2460 Å(3-5). In the present paper the molecular absorption band containing halogens has been investigated.

For the experiment, HITACHI 207 Atomic Absorption Spectrophotometer was used with no modification. In the case of measurement of molecular absorption spectra, deuterium lamp of the hollow cathode type, which was obtained from HAMAMATSU Co., was used as a continuous light source. As the electric power source for deuterium lamp, HITACHI 207-0100 High Voltage Power Source was utilized.

In atomic absorption spectrometry, it has been known that HCl interferes to the atomic absorption of indium in air-acetylene flame, although the precise mechanism of the interfering effect has not been known(6). The effect of HCl at higher concentration than 1 M to indium atomic absorption was first investigated in the present experiment using HNO_3 solution of indium as the reference, and the result is shown in Figure 1. As can be seen from Figure 1, indium signal is decreased as the concentration of HCl is increased. These interfering effects cannot be recovered even in nitrous oxide-acetylene flame as is also shown in Figure 1. The result shown above suggests the existence of indium-halogen compound in the flame. In fact, it has been found from the study of a high-frequency discharge that the diatomic molecule of InCl exists in the discharge tube and shows both

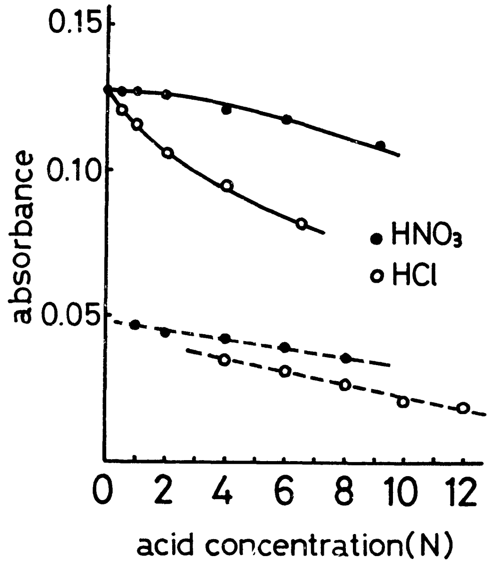


Figure 1. Chemical interfering effect of HCl to indium atomic absorption measured at 3039 Å in air-acetylene flame and in nitrous oxide-acetylene flame. (Concentration of indium: 20 μg/ml, ——: air-acetylene flame, ---: nitrous oxide-acetylene flame)

emission and absorption spectra(7). Moreover, the dissociation energy of InCl is known to be 4.50 ± 0.2 eV, which is larger than that of InO, 3.3 ± 0.5 eV(8). Therefore, the decreasing effect of HCl to indium may be at least partially explained by the formation of InCl in the flame.

In order to prove the above hypothesis of the formation of InCl in the flame, we measured the absorption band spectrum of indium in the regular ultraviolet region. The spectrum is shown in Figure 2, which was obtained by measuring absorbances at wavelengths with the interval of 1 or 2 Å, aspirating 0.2 M indium in 2 M HCl aqueous solution into air-acetylene flame. Sharp absorption bands are observed in the range from 2640 Å to 2720 Å, which is ascribed to the absorption bands of InCl. From the study of a high-frequency discharge, it has been known that InCl shows three systems of both emission and absorption bands(7). Among three systems, System C shows absorption only, degrades to the red, and has the bands at λλ2672 Å(0 - 0), 2694.7 Å(0 - 1), 2717.5 Å(0 - 2), 2740.6 Å(0 - 3) and λλ 2661.3 Å(1 - 0), 2683.7 Å(1 - 1). As is shown in Figure 2, the absorption bands obtained in this experiment are consistent with those observed in a high-frequency discharge. This fact indicates that the absorption bands observed in the present experiment are those of InCl. It is noted here that the diatomic molecule of InCl is produced even in the high temperature flame. Other two systems near 3600 Å(System A) and 3500 Å(System B) could not be observed in the present experimental conditions.

Numerous absorption lines in Figure 2 at 2957, 2932, 2858, 2851, 2837, 2775, 2752, 2714, 2710, 2601, 2560, 2521, 2467, 2459, 2429, 2398, 2389, 2358, 2339, 2277 Å and so on are considered to be indium atomic absorption lines, because the same lines were observed when 0.2 M indium in 2 M HNO_3 is aspirated into the flame under the same conditions as those shown in Figure 2. Among the absorption lines described above, those at 2752, 2714, 2710, 2601, 2560 and 2389 Å has been known

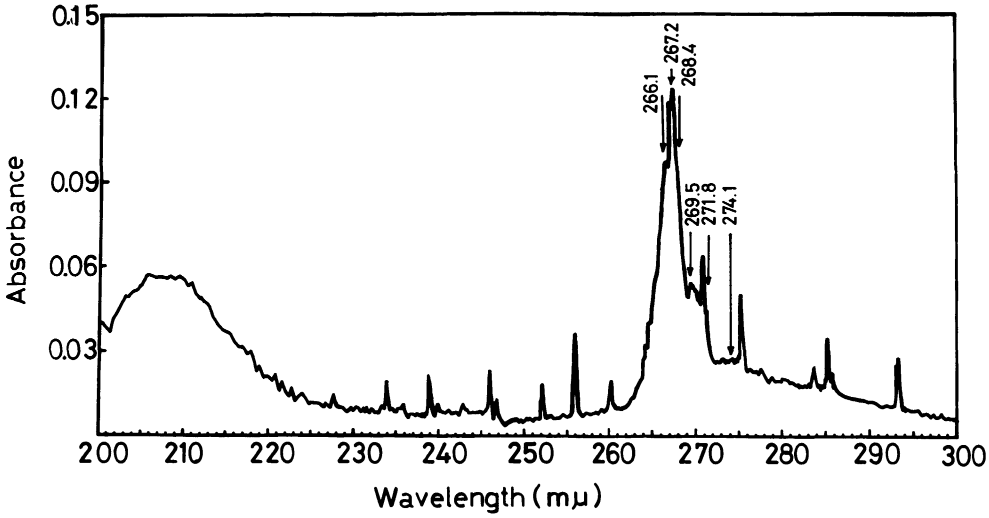
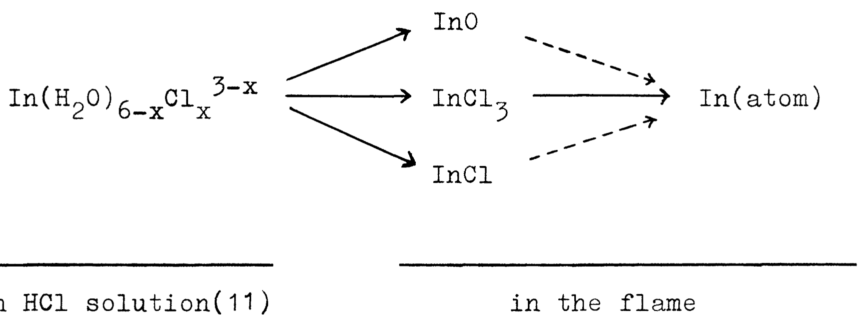


Figure 2. Atomic and molecular absorption spectrum of indium in the presence of HCl in air-acetylene flame.(Acetylene flow rate: 3.5 l/min, Air flow rate: 13 l/min, Flame height: 1 cm, Lamp current: 25 mA)

as the atomic resonance lines of In I and those at 2957, 2932, 2837 and 2775 Å as the atomic lines of In I(9). But the ionic lines of indium, In II, were not observed in Figure 2.

A very broad absorption band with the maximum at 2730 Å spreads from about 2600 Å to 3000 Å, and is partially overlapped with InCl bands in Figure 2. Since the band is also observed in the spectrum of indium in HNO_3, the absorption is ascribed to the band of InO. As for InO, the emission bands at 4500 - 4100 Å has been observed only in the DC arc, and is known to degrade to the red(10). It should be noted here that InO exists in air-acetylene flame, a relatively lower temperature medium. There appears another broad absorption band in the region shorter than 2200 Å, the assignment of which outside any oxide is under investigation.

The chemical interference of HCl to indium atomic absorption mentioned before, can now be explained by the formation of InCl in the flame, as the dissociation process into indium atom in the case of indium compounds in HCl solution being aspirated into the flames may be described as follows;



As is shown above, the study of molecular absorption spectra in the flame is very useful for the elucidation of the mechanism of the chemical interferences and the chemical reactions in the high temperature flames. The application of the molecular absorption bands of InCl to the determination of chlorine is in progress.

As the application of the molecular band to the determination of fluorine, Fuwa investigated the emission bands of CaF, SrF and BaF in the DC arc, and showed that those emission bands much distributed in the part of the fringe of the arc(12). Moreover, he showed that fluorine in various samples could be determined by the measurement of the emission intensity of CaF at 5292 Å. Although CaF band has been known to give both emission and absorption spectra(1), the molecular absorption of CaF at 5292 Å and in the regular ultraviolet region could not be observed in the present experiment, when about 1 M CaF_2 suspended in 50 % glycerine-water solution was aspirated into either air-acetylene flame or nitrous oxide-acetylene flame. The further studies of a possible absorption spectrum of alkaline earth fluorides in the flame as well as other systems of fluoride bands are also under investigation.

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