

Effect of Organic Solvents on the Atomic Absorption of Tin in Air-Hydrogen Flames - Part I

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Summary: The effect of organic solvents on tin absorption in air-hydrogen flames has been investigated. In present studies the effect of organic solvents found depended very much on the fuel/oxidant ratio of the flame. It has been found that solvents increased the tin absorption in fuel-lean flames while in fuel-rich flames they depress it. These studies significantly extend the present knowledge of behaviour of tin atoms in air-hydrogen flames. In this part of work the effect has been established by using various solvents, flames and metals and by changing other parameters such as flame height etc.

Introduction

It is well known fact that tin exhibits an exceptional behaviour in its flame chemistry and some basic mysteries related to this element have not so far been solved.

Tin is one of the elements which have a high tendency to form stable oxides in the flame. The high dissociation energy of tin oxide makes it impossible to thermally excite the tin atoms in air-hydrogen flames. In air-hydrogen flame with aqueous solutions, only a diffuse band at 4850\AA has been observed [1]. Gilbert [2] found that the lines emitted by tin were 1000 times more intense when an isopropanol solution was aspirated into an air-hydrogen flame than that when the solution was purely aqueous. This surprising change in tin emission due to organic solvents has been attributed to chemiluminescence; that is, some chemical reaction occurs in the flame, most probably between tin oxide and carbon or a carbon species giving rise

to excited tin atoms. Many other workers who have explored the phenomenon have agreed on the concept of chemical reduction of tin in the flame, but have proposed different reactions [3,4,5]. In other flames like oxygen-acetylene and air-acetylene the enhancement of tin emission due to organic solvents has been found relatively smaller as compared to that observed in air-hydrogen flame. Organic solvents have not been found essential for eliciting the tin emission when a carbon species was supplied by the flame gases [6].

Tin shows extra-ordinary behaviour not only in emission but also in atomic absorption. As a result of the high dissociation energy of tin oxide, only a small fraction of tin should be present in cool hydrogen flames as free atoms but contrarily, tin exhibits higher absorption sensitivity in hydrogen-supported flames. This fact has been commented by Walsh [7] and

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referred to as the "tin mystery" by Slavin [8]. De Galan and Samey [9] found an almost eight times higher degree of atomization for tin in the air-hydrogen flame than in the air-acetylene flame. What is even more intriguing is that in hydrogen-supported flames tin atomization seems to increase with decreasing temperature. Thus, with a direct injection burner, higher sensitivity was found in the hydrogen-air flame [10].

The first few workers who observed the increase in absorption sensitivity in cooler hydrogen flames did not give any explanation for this effect [11,12]. Lateron Nakahara [13] et al. and Rubeska [14] attempted to explain the enhancement by assuming the formation of free tin atoms in the reactions between tin oxide and free hydrogen atoms. Rubeska supported his assumption by quoting the work of Bulewicz and Padley [15] who showed that tin catalyses radical recombination reactions in hydrogen flames. Though tin shows highest sensitivity in hydrogen-supported flames, numerous puzzling interferences by a number of cations, anions and organic solvents have been observed on tin absorption in these flames [16,17,18]. The effect of organic solvents on tin absorption in hydrogen flames is particularly interesting because different workers reported different observations.

Harrison and Julliano [18] found that absorption by tin in an air hydrogen flame was severely depressed by the presence of organic solvents even in small quantities. Contrary to this, Gibson and co-workers [4] reported an enhancement of absorption with 50% isopropanol solution. Whereas, Vickers and colleagues, found no difference in the absorption of tin in aqueous and iso-propanal solutions of tin in the air-hydrogen flame [5].

While trying to develop a method for the estimation of tin in organo-tin compounds by atomic absorption spectroscopy [19] we unexpectedly found that the effect of organic solvents depended very much on fuel/oxidant ratio of the flame. This observation and the reports in the literature made the situation most interesting and it seemed worth exploring the effect in more detail. This investigation fell into two phases: First we established the effect by involving number of organic solvents, flames other than air-hydrogen and metals besides tin. In the second phase, we attempted to explore the chemistry behind these unusual changes. Results are being reported in the later parts.

Experimental

Apparatus

For emission and absorption studies the Perkin Elmer 305 Atomic Absorption Spectrophotometer was used for air-hydrogen and air-acetylene flames. Standard hollow cathode lamps were used for measuring the absorbance of tin and other metals. Readout in all cases was Servoscribe Chart Recorder.

Reagents

A 1000 ppm solution of tin was prepared by dissolving 0.5 g of AnalaR grade tin metal in 50 ml of hydrochloric acid and diluting to 500 ml with water. In most of the experiments absorption of 100 ppm tin solutions has been measured which were prepared by diluting 1000 ppm solution with known volumes of organic solvent and water. Flow rates of fuel and oxidant were measured from the monometer scales fitted on the flow control unit of the instrument. Different fuel/oxidant ratio of the flames were obtained by changing the hydrogen flow rate while air flow was kept constant.

Results and Discussion

Effect of various organic solvents on atomic absorption of tin in air-hydrogen flames.

The effect of a number of alcohols, ketones and other hydrocarbons on the tin absorption has been investigated at different fuel/oxidant ratios of the air-hydrogen flame.

Fig.1 shows the effect of butanone on the tin absorption at three different fuel/oxidant ratios. It is clear from the figure that adding solvent increased the absorption in fuel-lean flames whereas in fuel-rich flames it depressed the absorption. In between these two extremes, that is in stoichiometric flame the nature of the effect depended upon the solvent concentration in the sample solution. Other solvents had similar effect on the tin absorption except the magnitude of the change

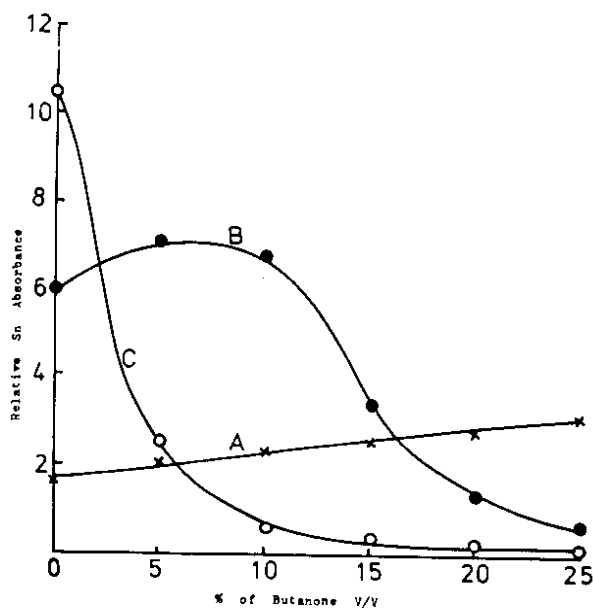


Fig.1: Effect of butanone on tin absorption in hydrogen flames. Sn $100 \mu\text{gml}^{-1}$ aqueous; Height above burner 2 mm; Wavelength 224.6 nm; Hyd/Air: A-1, B-1.5, C-2.

was different from solvent to solvent. The ketones quenched the absorption severely whereas ethanol and methanol depressed it mildly. Fig.2 gives an idea of the relative depression caused by methanol, n-butanol and butanone at fuel-oxidant ratio 2:1. As far as enhancement caused by various solvents in fuel-lean flame is concerned, ketones increased the absorbance more significantly as compared to alcohols.

Effect of burner height

The height above burner is another crucial parameter which has been thoroughly investigated. It had been found in previous work [19] that for aqueous solutions of tin the best absorption can be observed just above the burner tip which has also been supported by other workers [18].

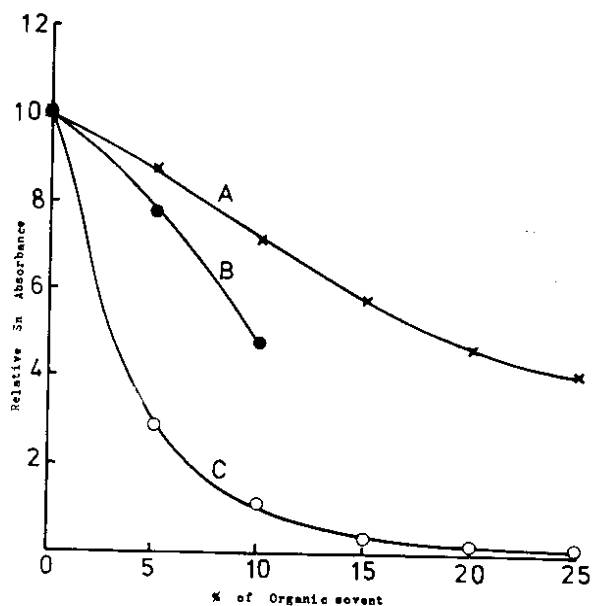


Fig.2: Relative effect of methanol, butan-1-ol and butanone. A-methanol; B-butan-1-ol; C-butanone; Other conditions same as for Fig.1.

Figure 3 indicates that the optimum tin absorption from the solution of different composition can be obtained by looking at different regions in the flame. Addition of butanone pushed the region of maximum absorption higher in the flame which is clearly understandable since with more solvent the gases will have travelled further up in the flame before sufficient air is taken in to complete the combustion.

Effect in air-acetylene flames

The effect of various organic solvents on the tin absorption has also been studied in air-acetylene flames. Here too, there was depression in reducing flames, enhancement in oxidizing flames and in intermediate flames the effect generally depended upon the solvent concentration. Figure 4 shows the effect of butanone on tin absorption at three different fuel/oxidant ratios of air-acetylene flames. Other solvents, dimethoxy ethane, acetone, ethanol and methanol also showed similar but very mild effect which could be explained by the difference in flame conditions at the two

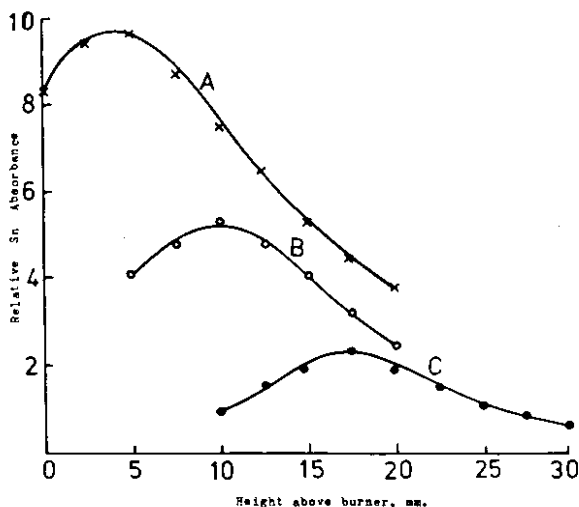


Fig.3: Variation in tin absorption with height above burner. Hyd/Air: 1.5, A, aqueous; B, 10% butanone; C, 25% butanone;

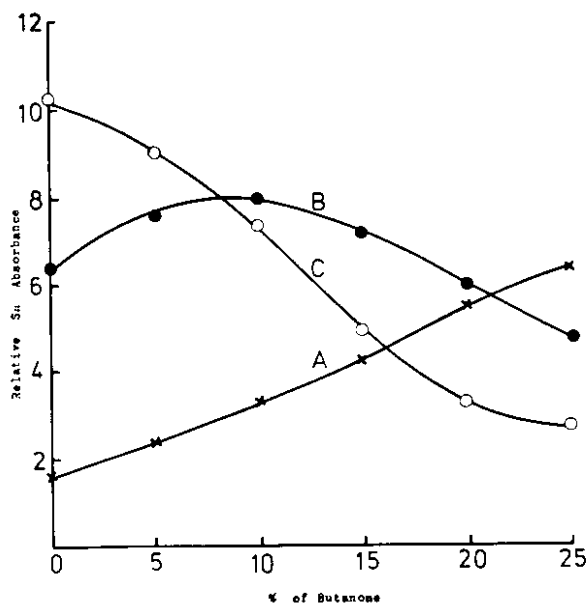


Fig.4: Effect of butanone on tin absorbance in air-acetylene flames.

Sn $100 \mu\text{gml}^{-1}$; Height above burner 2 mm, Ac/Air ratio A, 0.5, B, 0.75, C, 1.

extremes. The increase in absorption in oxidizing flame may be taken as the result of the conventional enhancing effects of the organic solvents whereas the gradual decrease in absorption in highly reducing flames is probably due to the dilution of flame gases and the reduction in flame temperature.

Earlier reports in the literature [20] have indicated that depression of the absorption by the addition of organic solvents was possible for several metals in highly reducing air-acetylene flame. However, the depressive effect found in this flame is far different from that observed in the air-hydrogen flame.

Effect on the Absorption of other metals.

The study of the effect has also been extended to a number of other metals besides tin. Effect of butanone

on the absorption of sodium, silver, copper, calcium and barium in air-hydrogen flames has been studied. Though the magnitude of the changes in each case was different, the general pattern was same. The absorption of sodium was not affected much even in highly reducing flames. The same was true for copper, and silver. The copper absorption, as shown in Fig. 5 was found least affected even in fairly rich hydrogen flames. The absorption of alkaline earth metals, calcium and barium was significantly affected by organic solvents. Both metals showed a similar behaviour to that of tin. The effect of butanone on calcium absorption is shown in Fig.6.

From this set of experiments it can be concluded that the effect of organic solvents on the atomic absorption of metals is more severe for those elements which have a pronounced tendency to form oxides in the flame. The reducing nature of flame probably prevents the oxide formation and helps in the atomization process.

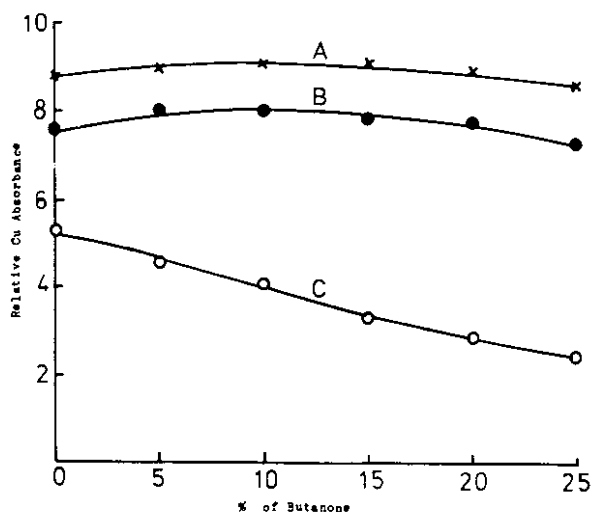


Fig.5: Effect of butanone on Copper absorption Cu 100 gm l^{-1} ; Wavelength 324.8, Hyd/Air A-1, B-1.5, C-2.

Effect on the emission of tin

As it was not possible to get a reasonable emission from aqueous solutions of tin in an air-hydrogen flame, an additional effect of 0-30% of butanone was studied on the emission of 50% ethanolic solutions of tin.

The effect in different hydrogen/air ratios is shown in Fig. 7: as the proportion of the solvent was increased the emission was enhanced in a lean flame and depressed in a fuel-rich flame, not unlike the picture found for absorption, but with some differences. The enhancement in emission by adding solvent was considerably greater than that found in the absorption of tin. On the other hand the depression caused by butanone on the emission was significantly less than that observed for absorption.

Perhaps it is possible to explain these effects on tin emission on the basis of physical properties. In addition flame temperature may also

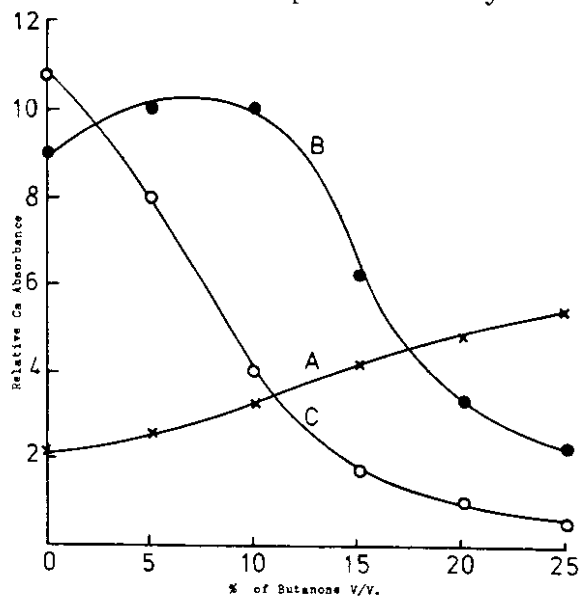


Fig.6: Effect of butanone on Calcium absorption. Ca 100 $\mu\text{gm l}^{-1}$; Wavelength 422.7 mm, Hyd/Air A,1; B, 1.5; C,2:

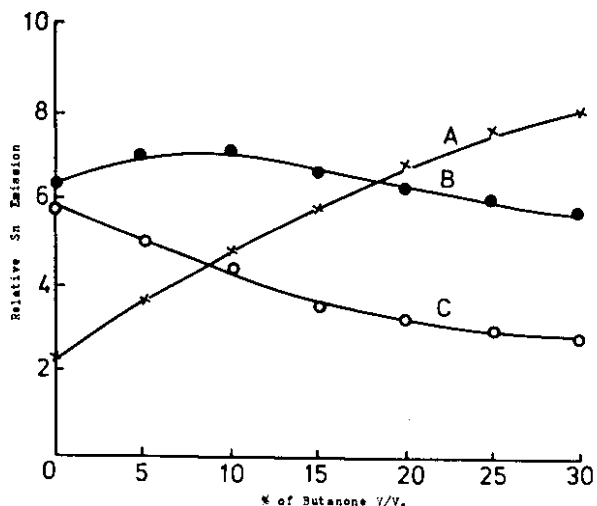


Fig.7: Effect of butanone on tin emission. Sn $100 \mu\text{gml}^{-1}$ in 50% ethano, Wavelength 284 nm; Hyd/Air A,1; B, 1.5, C, 2; Height above burner 2 mm.

be an accountable factor. Though it believed that in the air-hydrogen flame "Chemiluminescence" plays a major role in the emission of tin, even so, temperature may contribute through thermal dissociation of tin oxide and excitation of tin atoms to the total emission. It has also been stated that organic solvents increase the temperature of a lean flame and decrease it in a fuel-rich flame [4,21]. Another major factor responsible for the decrease in the emission could be the flame geometry.

The results, obtained so far, suggest that two types of effects are caused by organic solvents. One is the mild or general effect and other is strong or special effect which might be a result of general plus some additional effect. The general effect is found in the cases of tin absorption in air-acetylene flame, absorption of sodium, copper and silver and the emission of tin. In all these cases a mild depression has been found in fuel-rich flames and enhancement of almost same magnitude was observed

in fuel-lean flames. These common and mild changes are explainable to some extent.

The effect of enhancement in lean flames found in these cases may be attributed to the physical properties of the solvents. Low viscosity and low density of water-solvent mixture increase the rate of nebulization. Reduced surface tension helps the formation of finer spray droplets and a lower boiling point of the organic solvent cases the more rapid evaporation. All these properties enhance the absorption at low flow-rates. On the other hand at high fuel-flow rates the counteracting properties such cooling of flame, increase in flame velocity and size and extension of the region of observation probably more than offset the enhancing factors and cause a gradual depression. In spite of the general conclusion that the use of organic solvents improve the nebulization efficiency and rate of solvent evaporation etc. evidence can be find in the literature which clearly indicates a depression in the emission or absorption signal by the use of organic solvents in too strongly reducing flames.

Ramirez-Munoz [22] stated that excessively high sample intake rate may produce depression signals by a cooling effect. Feldman and co-workers [23] experienced this effect during the determination of manganese in an air-hydrogen flame. For air acetylene flames Lemonds and Mc Clellan [20] strictly recommended low flow-rates when organic solvents like ketones and esters were being used. In a recent publication Cresser [24] pointed out that an increase in aspiration rate, such as that which may be obtained on changing from an aqueous to an organic sample solution, does not in itself mean that a corresponding impro-

vement will be observed in the sensitivity. He further adds that it may in fact lead to a decrease in nebulization efficiency.

This probably explains to some extent the mild depression found in extremely fuel-rich flames for the cases mentioned at the start of this discussion.

Next is the class of elements which form refractory oxides. Atomic absorption of these elements is severely depressed by organic solvents in fuel-rich air-hydrogen flames. These metals just as calcium barium and tin etc have a common tendency to form oxides in the flame, in which case the thermal dissociation of their oxides seems difficult in a cool air-hydrogen flame, though unexpectedly they do exhibit a remarkable absorption in this flame. This suggests that hydrogen must play some chemical role in addition to the thermal atomization. These elements show similar behaviour in flames in the presence of organic solvents. Calcium, barium and tin showed similar behaviour but our attention will be largely confined to that of tin in this work.

The most intriguing issue in the present discussion is severe depression in the tin absorption by organic solvents. Just as the abnormal tin absorption can not be attributed to the poor thermal atomization of the hydrogen flame, similarly adverse effects of organic solvents on the tin absorption can not be explained simply by taking physical properties and temperature changes into account. Some additional factors were thought to be involved for the changes observed in the case of tin therefore, a detailed study of these factors was carried out and the results are being presented in later Parts. However at this stage

this can be recommended safely that fuel/oxidant ratio plays a very crucial role in getting reproducible results when organic solvents are being used with air-hydrogen flame especially for oxide forming elements like tin.

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