

Effect of Organic Solvents on the Atomic Absorption of Tin in Air-Hydrogen Flames: Interconal Zone and Flame Geometry (Part-II)

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Summary: On aspirating organic solvents into an air-hydrogen flame two significant effects have been observed: first the flame dimensions were considerably changed and second, a fairly luminous greenish-blue zone appeared in the flame. Various parameters related to this internal zone were investigated and it has been found that the internal zone has a significant role in the depression observed in tin absorbance by organic solvents.

Introduction

In continuation to our studies related to the exploration of the facts behind the severe depression caused by organic solvents on tin absorbance in air-hydrogen flames [1,2], this paper describes some visual changes observed in the flame on aspirating organic solvents and correlates them with the depression in tin absorbance.

Often organic solvents enhance the atomic absorbance of an element due to their favourable effects on physical and combustion properties of sample solution [3,4]. In certain cases organic solvents cause deterioration in the absorption sensitivity [5,6]. This decrease may be attributed to some undesirable changes in one or more physical properties of the solution or in flame temperature or due to some thermochemical reaction in the flame [7].

Though flame geometry is one of the important factors which can be considerably affected by organic solvents and cause a depression in absorption signal, only a few workers have discussed the possible influences

of changes in flame geometry upon absorption sensitivity when organic solvents are nebulized. Szivos [8] et.al. investigated the correlation between changes in the geometry of an air-acetylene flame and absorption sensitivity. They also studied the effect of various organic solvents on the height of internal reaction zone. Another group of workers, Fassel [9] et.al., has also reported some spectroscopic observations on the effects of the primary reaction zone of premixed oxy-acetylene flames.

During our work on developing a method for the estimation of tin in organo-tin compounds by atomic absorption spectroscopy [10], we found that, on aspirating organic solvents into an air-hydrogen flame, a fairly luminous bluish-green zone appeared at the burner slot. Later experiments proved a direct relationship between this internal zone and the depression in tin absorbance by organic solvents. Various parameters related to this zone are discussed in the present work.

Experimental

Equipment:

A Perkin Elmer 305 atomic absorption spectrophotometer with 10 cm single slot burner was used for these studies. To measure the height of various zones in the flame an additional 25 cm stainless steel scale was fitted on one side of the burner. Air and hydrogen flow-rates were controlled by the flowmeters provided with the instrument. Different hydrogen/air ratio flames were obtained by changing the hydrogen flow-rate while air pressure was kept constant.

Reagents:

Organic solvents obtained from BDH (British Drug House) and E. Merck were used without further purification. A $1000 \mu\text{g ml}^{-1}$ solution of tin was prepared by dissolving AnalaR Grade tin metal in the minimum quantity of hydrochloric acid and diluting with water. Absorbance from $100 \mu\text{g ml}^{-1}$ solutions was measured. These were prepared by diluting the $1000 \mu\text{g ml}^{-1}$ tin solution with appropriate volumes of organic solvents and water.

Flame Geometry:

The vertical cross-section area of the flame was measured with the help of an additional scale fitted along the burner. As shown in Fig. 1, there was almost a linear relationship between the flame height and the hydrogen flow-rate when the air pressure was kept constant. Though due to the limitations of the instrumentation it was not possible to measure the flame thickness exactly, it was obvious that increasing the fuel or oxidant flow-rate increased the flame thickness, especially 1-2 cm above the slot.

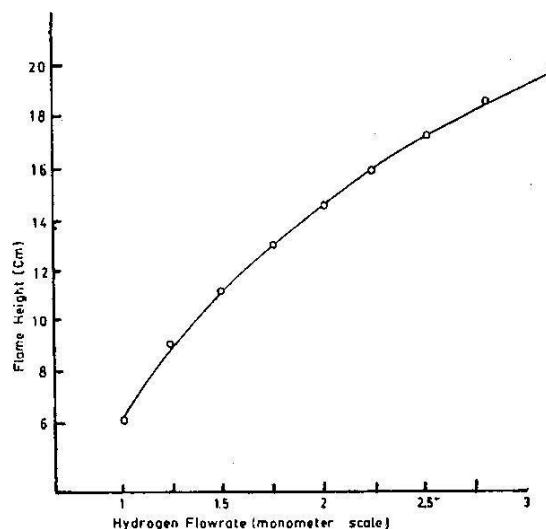


Fig. 1: Effect of hydrogen flow-rate on flame height.

The vertical height of the flame remained almost unchanged in spite of the nature and concentration of the solvent; however both of these factors changed the flame thickness significantly. Higher concentrations of organic solvents increased the flame thickness considerably. Fig. 2 gives a rough idea of approximate flame dimensions at various fuel/oxidant ratios when different concentrations of butanone were aspirated.

One simple conclusion which can be drawn from these observations is that the increase in cross-sectional area of the flame due to increasing hydrogen flow and aspirating an organic solvent decreases the concentration of analyte per unit cross-sectional area of the flame, i.e. a given mass of analyte will be spread over a larger volume which would result in a depressive effect on the absorption sensitivity.

Interconal Zone:

It was noticed that when an aqueous solution was sprayed into an air-hydrogen flame at low pressure of

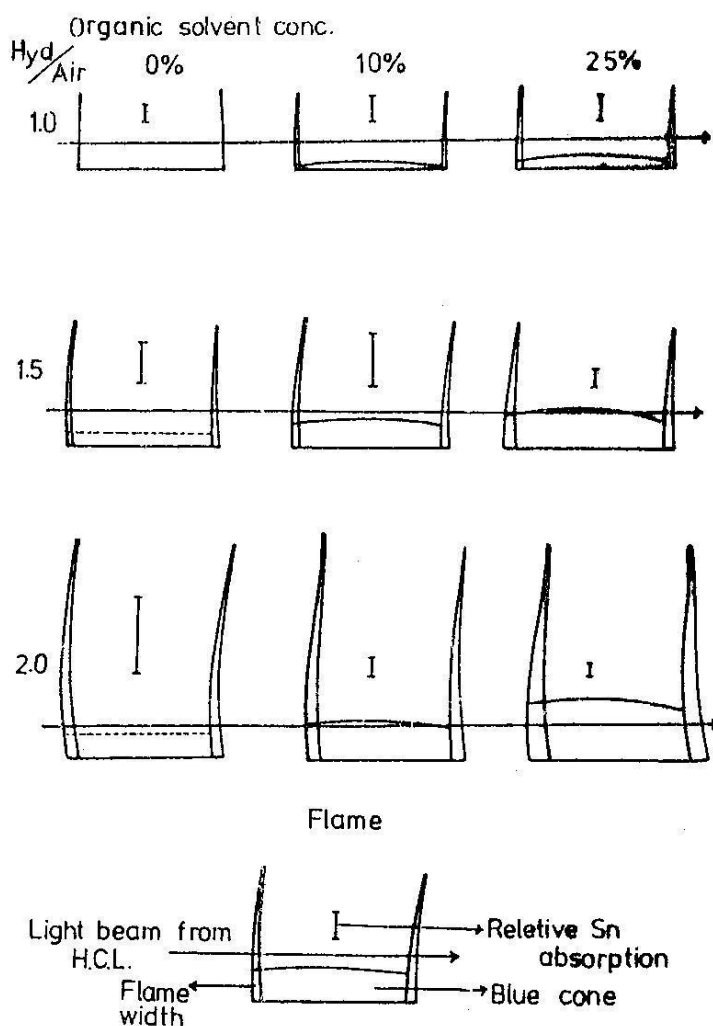


Fig-2: Relative effects on flame dimensions and tin absorption by aspirating various concentrations of butanone in different Hydrogen/air flames.

flame gases, the flame remained uniform and almost colourless. However, at high fuel flow-rates, a slightly darker primary reaction zone appeared over the burner slot, the height of which depended upon both fuel and oxidant flow-rates. In the presence of organic solvents a fairly luminous greenish-blue cone appeared in place of the darker zone. The height of this greenish-blue zone in the flame depended upon the flow-rate of flame gases, the concentration of the organic

solvent and the nature of the organic solvent. Each factor affected the size of the internal zone when the other two factors were kept constant.

The effect of various concentrations of butanone on the interconal zone height at a fixed fuel/oxidant ratio is shown in Fig.3(A). Similarly Fig.3(B) shows the variation in the interconal zone height on aspirating 25% (by volume) solutions of different organic solvents. The relative effect

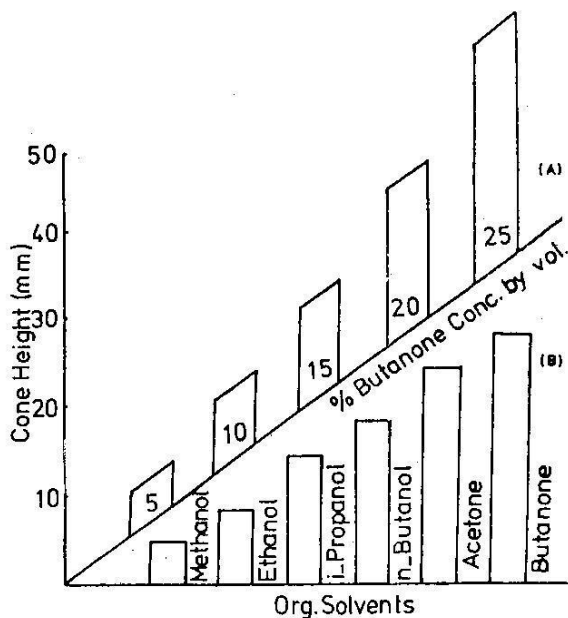


Fig.3: (A); Effect of different concentrations of butanone on internal cone height. (B); Effect of 25% solutions of different solvents on internal cone height. Hydrogen/air ratio in both cases: 2.

of various concentrations of butanone on the size of the interconal zone at different fuel/oxidant ratios has also been given in Fig.2.

Interconal Zone and Tin Absorbance:

To check on the possible effects of the interconal reaction zone on tin absorbance $100 \mu\text{g ml}^{-1}$ solution of tin was aspirated and the absorbance was measured over a range of flame conditions. In Fig.2 an attempt is made to give a comprehensive overview of the results.

In addition to the general expansion of the whole flame, the formation and lengthening of the internal blue zone, due to increasing hydrogen flow and solvent concentration, probably affects the tin determination more severely because

the zone extends into that part of the flame where atomization and measurement of tin normally take place. Extension of this region obviously affects the measured tin absorbance adversely. Fig.2 also illustrates the fact that the tin absorbance was depressed more seriously when the blue zone extended above the light beam from the source or the zone of absorbance measurement and less depression was observed when the light beam passed over the edge of the zone. This suggested that by aspirating organic solvents into fuel-rich flames the region of maximum absorbance is pushed higher in the flame and lies around the upper edge of the blue zone. The idea gets further support from the fact that the different solvents increased the height of internal zone in the same order in which they depressed the tin absorbance as found in previous experiments [2,5].

Conclusion

As it has been suggested in the literature [11] and confirmed by these studies, in addition to causing physical spreading of analyte over a larger volume of the flame, the internal greenish-blue reaction zone may affect the thermal and chemical atomization of the analyte. The overlapping of the measurement region by the interconal zone may have different effects upon different elements. The elements whose atomization depends critically upon the temperature, height above burner and/or some chemical reaction in the flame may be more seriously affected and most probably tin is one of such elements.

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