# Effect of Organic Solvents on the Atomic Absorption of Tin in Air-Hydrogen Flames: Spectroscopic studies of flame species (Part III)

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**Summary:** By aspirating organic solvents into air-hydrogen flame, numerous carbon containing radicals were produced in the flame. A few of them like $C_2$, and $CH_3$ were identified by their emission and absorption bands in the flame spectra and their relative strengths were determined at different flame conditions. The absorption of methyl radicals at 216 nm was found closely related to the depression in the tin absorption. By measuring the free hydrogen atoms and hydroxyl radicals by emmission, it has been found that the concentration of atomic hydrogen was affected by organic solvents in a similar manner to the tin absorption signal.

## Introduction

In continuation to our studies related to investigate the facts responsible for the severe depression in tin absorption by organic solvents in air-hydrogen flame [1-3], this paper presents the results of spectroscopic investigations of some flame species. An attempt is also made to explain the unusual depression on the basis of evidences obtained from these studies.

A number of carbon species have been identified in the emission spectra of organic solvents in hydrogen flames. Gaydon [4] made preliminary but extensive investigations in this field. Robinson and Smith [5] studied the emission spectra of a number of organic solvents in an oxy-hydrogen flame and observed some terminal combustion products. The radicals produced by organic solvents play an important role in the atomization and excitation of an element in the flame. The surprising increase in tin emission due to organic solvents, first reported by Gilbert [6], has been attributed to "Chemiluminescence": that is some chemical reaction occuring in the flame, most probably between tin oxide and carbon or carbon species giving rise to excited tin atoms. A number of other workers also investigated the enhancement effect of organic solvents in tin emission. Buell [7] found that the chemiluminescent spectrum of tin in alcohol solution was weaker in oxy-hydrogen flames than in the air-hydrogen flames. Gibson [8] et al. also explored some useful aspects of the phenomenon and confirmed the results of Buell and Gilbert. Vickers [9] et al. made a comprehensive study of the atomization and excitation process for tin in different hydrogen flames. These authors supported the chemiluminescence theory and discussed a number of possible reactions.

With this background it would not be surprising that the severe depression in tin absorption by organic solvents is a result of some thermochemical reaction in which one or more organic radicals are involved. To

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explore this possibility we spectroscopically investigated the various flame species produced by organic solvents at different flame conditions.

## Experimental

*Equipment:*

For emission and absorption studies a Perkin Elmer 305 Atomic absorption spectrophotometer was used. This instrument was basically designed for atomic absorption spectroscopy but emission can also be measure by switching it to emission mode. A deuterium lamp was used as a continuous source to measure the absorbance of methyl radicals. An additional low speed motor was attached to the wavelength control of the instrument to scan the spectra.

*Reagents:*

Organic solvents obtained from BDH and E. Merck were used without further purification. Emission of 1000 ppm metal (Sn and Cu) solutions was measured which were prepared from Anala R Grade metals. Phosphoric acid was used for checking the HPO emission.

## Discussion

*Flame Spectrum:*

To identify the principal flame species, emission spectrum of the flame was scanned with and without organic solvents. In Fig.1 the spectrum of the air-hydrogen flame with 25% v/v butanone solution is reproduced. The emission of OH radicals around 310 nm predominated over other species observed in the spectrum. Among the Swan bands of $C_2$, the band at 516 nm was fairly intense compared to the other bands at 473 and 563 nm. A significant emission from CH was also observed at 431.5 and 438 nm.

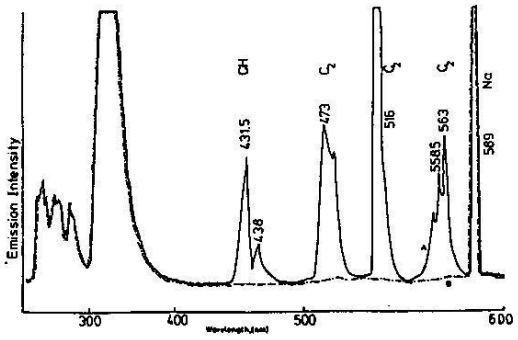


Fig.1: Emission spectra of the air-hydrogen flame.
A---25% Butanone v/v in water;
B---Blank (water aspirared)

It was observed that different concentrations of a certain organic solvent did not have much effect on the emission of $C_2$ and CH radicals except causing a slight increase with increasing concentration of solvent. However the same concentration of different solvents produced significantly different emission of the carbon species. The maximum effect on the emission intensities of the $C_2$ and CH bands was observed by varying the fuel/oxidant ratio of the flame.

Relevant literature confirms the finding of this part of the work. Gilbert [10] concluded that carbon compounds sprayed into an oxy-hydrogen flame produced a number of radicals which seemed to play an important role in the chemiexcitation of various compounds. Robinson and Smith [5] also studied the combustion of organic solvents in an oxy-hydrogen flame and observed that addition of hydrocarbon solvents to the flame produced significant change in flame spectrum.

*$C_2$ and CH Radicals:*

Emission of $C_2$ and CH radicals at 516 nm and 431 nm respectively was measured for different flame conditions. Fig.2 and 3 reflect the emission of both radicals when 5-25% v/v butanone solutions were aspirated into the flame at different fuel/oxidant ratios.

A very faint $C_2$ emission intensity was observed when dilute solutions were used in a lean flame but it became reasonably strong when fuel/oxidant ratio reached 1.5. At extremely high hydrogen flow-rate the $C_2$ emission became negligible. The emission profibes of CH emission were slightly different: high concentrations of butanone in a fuel-lean flame produced the maximum emission which decreased with increasing fuel flow-rate and finally at a fuel/oxidant ratio 2 it also became almost negligible.

The $C_2$ and CH emission intensities recorded for different solvents were in the order: butanone > acetone >n-butanol > iso-propanol > ethanal >methanol. The common feature, observed in the emission of $C_2$ and CH that both became practically negligible when concentrated solutions were aspirated into a fuel-rich flame, suggests the possibility of some chemical reactions taking place between these species and hydroxyl or hydrogen radicals.

*$CH_3$ Radicals:*

In an attempt to scan the absorption spectrum of the air-hydrogen flame while aspirating 25% butanone, it was incidently found that the solvent shows a substantial absorption due to methyl radicals at 216 nm. As

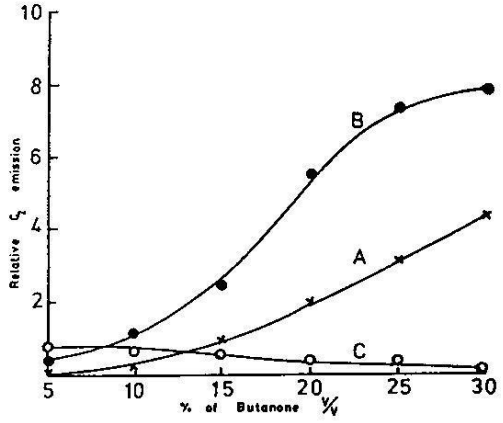


Fig.2: $C_2$ emission in different air-hydrogen flames. Wavelength:516; Height above burner: 3mm; Hyd./Air ratio: A-1, B-1.5, C-2.0.

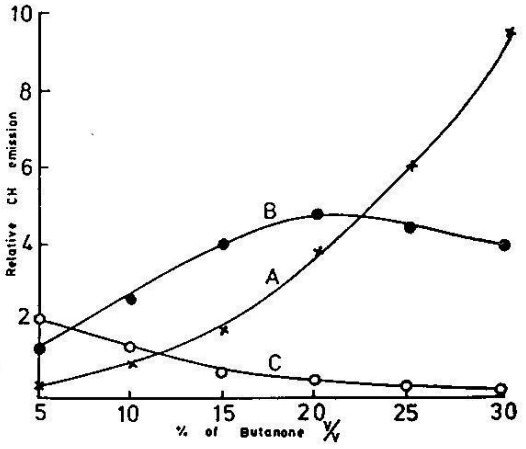


Fig.3: CH emission in different air-hydrogen flames. Wavelength: 431 nm; other conditions as for Fig.2.

illustrated by Fig.4, absorption of methyl radicals was measured under various flame conditions.

The absorption remained inconsiderable in lean flames at all concentrations of butanone. In a medium flow of hydrogen the absorption started to rise when the concentration of butanone reached 15% and in the same flame the maximum absorption was observed with 25% v/v

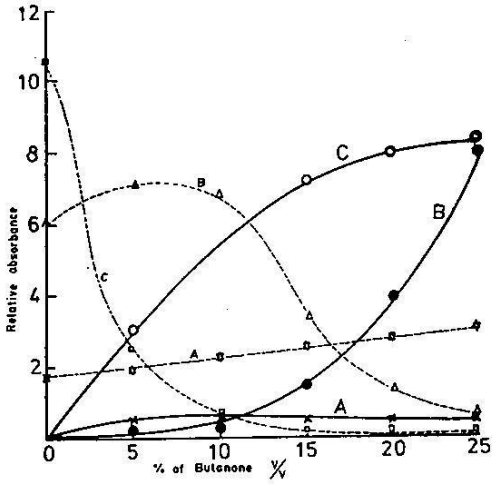


Fig.4: Variations in tin absorbance at 224.6 nm and absorption due to $CH_3$ radicals at 216nm.,--Tin absorption,--$CH_3$ radical absorption Hyd./Air ratio: A-1,B-1.5, C-2.0; Sn:100 g $ml^{-1}$.

of butanone. In a fuel-rich flame the absorption of $CH_3$ radicals rose abruptly with the increase in concentration of butanone.

By comparing the variation in methyl radical concentration and the depression of tin signal (Fig.4), one can easily find a correlation between the two. In the lean flame the methyl radical concentration is negligible and no tin depression is observed. In a medium flame $CH_3$ radical absorption starts to increase from 15% v/v butanone, just when the depression of tin absorption signal becomes evident Lastly in fuel-rich flame the methyl radical concentration increases rapidly and the same happens with the depression in tin signal. Fig.5 shows the correlation clearly between methyl radical concentration and the depression in tin absorption by the same concentrations of butanone.

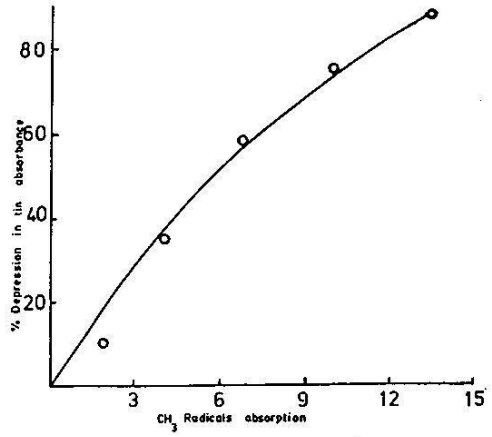


Fig.5: Correlation between depression in tin absorption and $CH_3$ radicals absorption. Sn: 100 g $ml^{-1}$; Hyd./Air ratio: 2; Butanone concentrartion 2-10%.

Moreover the methyl radical production from different solvents was found to be in the same order as their depressive effect on the tin absorption (Table 1 and Fig.6). The case of formic acid would be worth mentioning. As reported [11], this solvent had no diverse effects on the tin absorption and in this work it was found that the methyl radical concentration was practically zero when solutions of formic acid were aspirated.

These findings suggest that methyl radicals are involved in some reaction which directly or indirectly results in a severe depression in tin absorption.

*OH Radicals:*

OH Radicals show a strong emission around 310 nm but it was not possible to measure absolute concentrations, only relative values could be obtained. As shown in Fig.7 there is a significant variation in the concentration of OH radicals for

Table-1: Comparison of the effect of organic solvents on tin absorbance.
(as reported by Harrison and Julliano [11]).

| Organic Solvent | %age Change* |
|---|---|
| Methanol | - 8.8 |
| Ethanol | -19.1 |
| n-Propanol | -61.4 |
| Iso-Propanol | -61.4 |
| n-Butanol | -42.7 |
| t-Butanol | -73.7 |
| Acetone | -84.1 |
| Methyl-Ethyl Ketone | -90.0 |
| Formic Acid | + 3.7 |
| Acetic Acid | - 7.2 |
| Propionic Acid | - 9.7 |

$$* \% \text{ change} = \frac{\text{Absorbance (4\% Org.Soln)} - \text{Absorbance (aq.soln)}}{\text{Absorbance (aq.soln)}} = 100$$

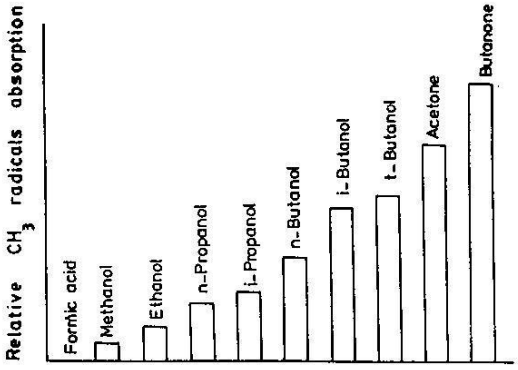


Fig.6: Relative absorption due to $CH_3$ radicals by 10% v/v solutions of various solvents.

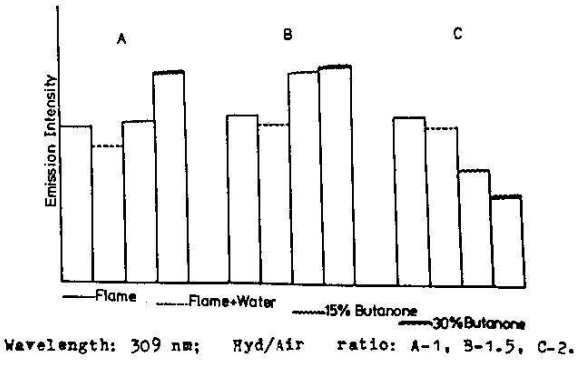


Fig.7: Variation in OH radicals emission with hydrogen flow-rate and beutanone concentration.
Wavelength: 309 nm; Hyd/Air ratio: A-1, B-1.5, C-2.

different fuel/oxidant ratios and with different concentrations of butanone.

In lean flames the addition of organic solvent increased the OH radical concentration whereas in fuel-rich flames butanone depressed the OH emission.

The emission of OH radicals has been used both for the determination of OH concentrations and for the measurement of the flame temperature, therefore it is equally possible that the variation in OH emission may be due to the changes in flame temperature when an organic solvent is aspirated rather than any chemical reaction [12]. Moreover the emission intensity of OH radicals in flames has been usually attributed to chemiluminescence and explained by the reaction proposed by Gaydon [13].

$$CH + O_2 \text{ ----- } CO + OH^*$$

Therefore the emission from OH radicals can not be considered as simple molecular emission unaffected by other species. More likely the variation in OH radical emission is either due to change in the thermal conditions of the flame or to a shift in H and OH equilibrium caused by organic solvent. In literature it has already by reported [14] that an increased in hydrogen flow severely depressed the hydroxyl radical emission when benzene was aspirated into oxy-hydrogen flame.

*H Atoms:*

To monitor the concentration of H radicals in the flame, emission of copper hydride was measured at 428 nm with and without addition of different concentrations of butanone and at three different fuel/oxidant ratios. Fig.8 shows the emission profiles of copper hydride. Parallel results have been obtained when molecular emission of HPO and SnH was checked at 526 nm and 609.5 nm

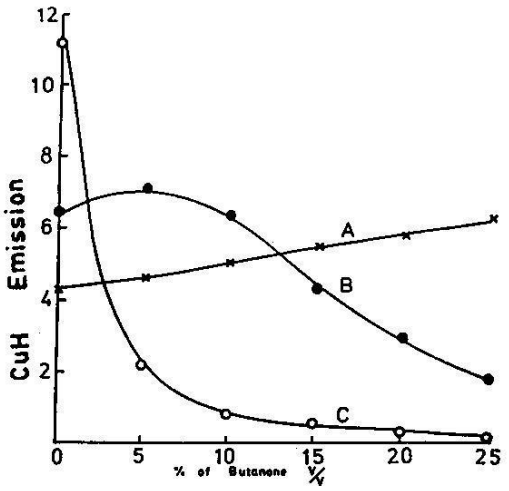


Fig.8: Variation in CuH emission with butanone concentration in air-hydrogen flames. Hyd./Air ratio; A-1, B-1.5, C-2.0; Cu 100 g $ml^{-1}$.; Wavelength: 428 nm.

respectively under the same conditions as used for CuH. The use of all these species was based on the idea that their formation and obviously then their emission would be a proportional measure of atomic hydrogen concentration. The CuH band emission at 428 nm has already been used to measure the atomic hydrogen concentration [15].

The results from this study showed that the effect on the emission from all three hydride species by organic solvents at various hydrogen flow-rates was, firstly similar in all cases and secondly, unbelievably parallel to the effect on the tin absorption signal (Fig.4). This similarity strongly suggests that hydrogen atoms play a key role in the effect of organic solvents on tin absorption and more likely they help in tin atomization directly or indirectly.

*SnO Radicals:*

A number of research workers believed that in hydrogen flames either tin oxide is directly reduced to tin atoms by atomic hydrogen or at some stage tin hydride is formed which breaks down to tin atoms [16-18]. To explore this, molecular emission of SnO at 348.5 nm has also been checked under the same conditions which had been used for the tin hydride emission work. Fig.9 shows the emission profiles of tin oxide with different concentrations of butanone and different fuel/oxidant ratios.

The results obtained partly confirmed the proposed theory as tin oxide gave maximum emission in a lean flame and minimum in a fuel-rich flame, whereas for hydride emission the reverse had been found. This proves that in hydrogen rich flames tin hydride forms at the cost of tin oxide. Keeping in view the effect of organic solvents on the tin absorption, an increase in tin oxide emission might

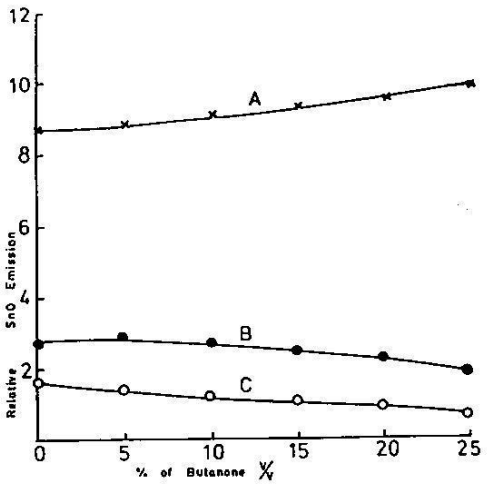


Fig.9: Variation in SnO emission with butanone concentration in air-hydrogen flames. Sn:100 g $ml^{-1}$.; Wavelength:348.5 nm.; Hyd./Air ratio: A-1, B-1.5, C-2.0.

have been expected when organic solvents were aspirated into a rich hydrogen flame, but in fact no significant change in emission intensity was observed.

## Conclusion

By spectroscopic studies of the air-hydrogen flame it has been found that by nebulizing organic solvent mixtures numerous carbon-containing radicals such as $C_2$, CH and $CH_3$ were produced. The absorption of methyl radicals at 216 nm was found closely related to the depression in the tin absorption i.e. the depression was most severe when methyl radicals were present in maximum concentration in the flame.

On the other hand by measuring free hydrogen atoms and hydroxyl radicals concentration by emission it was found that the concentration of atomic hydrogen was affected by organic solvents in a similar manner to the tin absorption signal. It seems that in the absence of organic solvents free hydrogen atoms help tin atomization but when organic species like methyl radicals are produced in the flame by the combustion of organic solvents, they deplete the free hydrogen which ultimately results a depression in the tin absorption.

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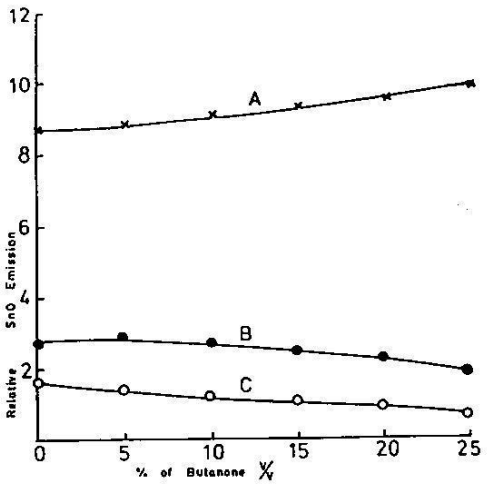


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