

Effect of Organic Solvents on the Atomic Absorption of Tin in Air-Hydrogen Flame: Analyses of Flame Gases (Part-IV)

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Summary: By aspirating butanone into air-hydrogen flame numerous species were produced in the flame. To detect various terminal species and monitor their concentrations the gases from different parts of the flame were pumped into gas chromatograph. The major products detected by this method were light hydrocarbons, oxides of carbon, ketones, alcohols and flame gases like nitrogen, oxygen and hydrogen. The variation in concentration of these species with hyd/air ratio of the flame has been checked.

An attempt, based on the evidences obtained in these studies, is made to explain the unusual depression in tin absorption caused by organic solvents in air-hydrogen flame.

Introduction

On aspirating organic solvents numerous carbon species are produced in hydrogen flames. Many workers studied the emission and absorption spectra of the flames containing hydrocarbons and detected a number of intermediate and terminal combustion products.

Robinson and Smith [1] aspirated organic compounds into an oxy-hydrogen flame and investigated the emission spectra. These authors observed some emission bands in the infrared region which they attributed to larger molecular fragments. McCrea and Light [2] identified C_2 and CH emission bands in air-hydrogen and oxy-hydrogen flames when solutions of different hydrocarbons in methanol were nebulized. Limited area flame spectroscopy, a technique in which only a selective region of the flame

is observed at a given time, has been utilized by Buell [3] in various studies of spectral emission from combustion of organic solvents. Recently Sturgen and co-workers [4] analysed the gases from a high temperature graphite furnace by gas chromatography and identified CO_2 , CH_4 , C_2H_4 , C_2H_2 and C_2H_6 .

During our work related to investigate the factors responsible for the severe depression in tin absorption by organic solvents [5-7], the solvents were aspirated into air-hydrogen flames and a number of radicals like C_2 , CH, CH_3 , H and OH were identified by emission and absorption measurements. Their relative concentrations have also been measured spectroscopically at different flame conditions [8]. As it was not possible to detect and quantify spectroscopically many of the intermediate species and particularly the

final products, present in the flame we decided to analyse flame gases by gas chromatography. In this communication the results of the chromatographic analyses of the gaseous products from the flame are presented.

Experimental

Butanone - water solutions of different concentrations were aspirated to a Perkin Elmer 305 atomic absorption spectrophotometer. A stainless steel capillary tube of 1mm diameter was used to suck the gases from the different parts of the flame. The gases were then directly pumped into a loop attached to the gas sampling valve of a gas chromatograph. A cooling coil and a drying tube with magnesium perchlorate were also provided to freeze the possible reactions and to remove the water vapour from the gas samples. A schematic diagram of the assembly is shown in Fig.1.

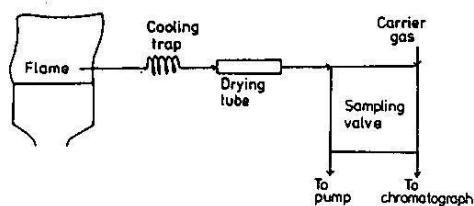


Fig.1: Assembly used for chromatographic analysis of flame gases.

Before running the samples from the flame expected individual gases and their mixtures were injected to note retention times for different gases. In the case of volatile liquids, vapours of respective compounds were used for calibration. Though absolute quantitative determinations of each flame component were difficult because of air from atmosphere, relative concentrations were measured at different flame conditions and from different flame regions.

Different instruments, columns and conditions had to be used for different sets of flame species. Details of the conditions are given in Table 1.

Results and Discussion

Hydrocarbons:

A number of hydrocarbons: CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , C_3H_6 , and C_2H_2 were detected in flame gases when aqueous-butanone solutions were nebulized. A typical chromatogram of these compounds is shown in Fig.2. It has been found that concentration of hydrocarbons depended on three main factors: height above burner, hyd/air ratio and concentration of butanone.

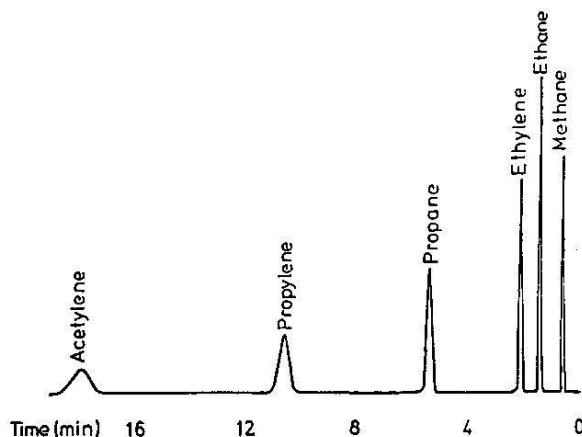


Fig.2: Chromatogram of light hydrocarbons in flame gases.

The concentration profiles of methane with height above burner slot and at different hyd/air ratios are shown in Fig.3. At each hyd/air ratio the concentration increased with increase in distance between the sampling capillary and burner slot, reached at a maximum and then started to decline. Similar concentration pro-

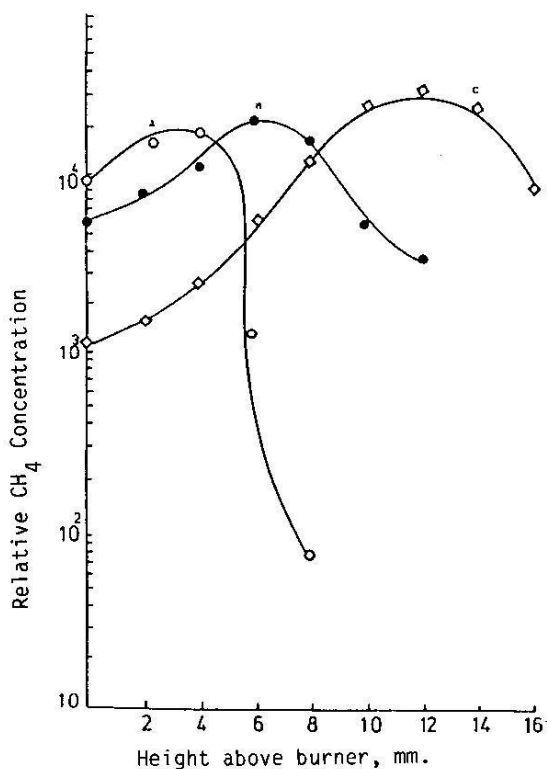


Fig. 3: Variation in CH_4 concentration with height above burner. 25% Butanone was aspirated into Air/Hyd. Flame, Hyd/Air ratio : A-1, B-1.5, C-2.

files have been obtained for other hydrocarbons except acetylene. However the hydrocarbons were different in concentration and their maximum concentrations lie in different regions of the flame. A slow rise and fall in concentration profiles of hydrocarbons suggested that these species were formed slowly by recombination of radicals in the lower region of the flame and then most probably oxidized in the higher regions where enough oxygen was available from the atmosphere. As represented in Fig. 4, the case of acetylene has been found an exception, the concentration of this gas did not drop even at 25 mm high in the flame.

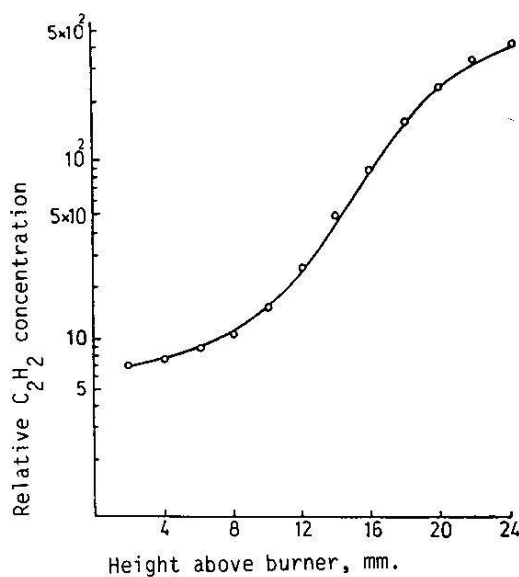


Fig. 4: Variation in C_2H_2 concentration with height above burner. Butanone aspirated : 25% Hyd/Air ratio : 1.5.

Hydrogen flow at a constant air pressure is another important parameter which influenced the formation of hydrocarbons and also shifted the region of maximum concentration in the flame. In flames with luminous blue cone, 99% of the methane lies in this cone. The same was found for other hydrocarbons. In lean flames the region of maximum hydrocarbon concentration exists very close to the burner slot whereas in fuel-rich flames hydrocarbons have been spread over a 15 mm region above the burner.

Fig. 5 shows the effect of hyd/air ratio and the butanone concentration on the levels of hydrocarbons. It is interesting that in lean flame the concentration of hydrocarbon is very low at 5 mm above the burner slot even when 25% v/v butanone solution is aspirated. The hydrocarbon concentration along horizontal axis at various

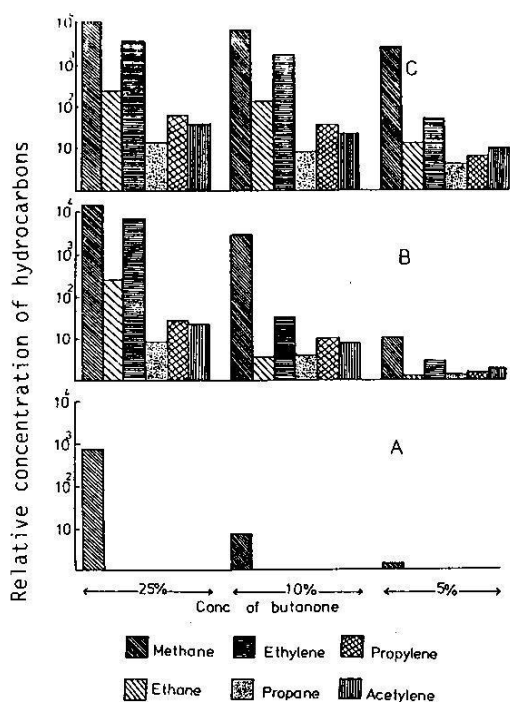


Fig.5: Variation in the concentration of hydrocarbons with butanone and hydrogen flow-rate. Hyd/Air ratio: A-1, B-2.5, C-2 Height above burner - 4mm.

heights has also been checked. Horizontal distribution of methane at different heights in the flame is shown in Fig.6. The maximum in all cases, was found just in the middle of the flame with a sharp fall in concentration along the horizontal axis across the burner slot.

Ketones and Alcohols:

An attempt was made to look for polar organic compounds in the flame gases. The compounds detected by aspirating 25% butanone solution, were unburned butanone, methanol, acetone and formaldehyde.

The height profiles of these compounds in a medium air-hydrogen

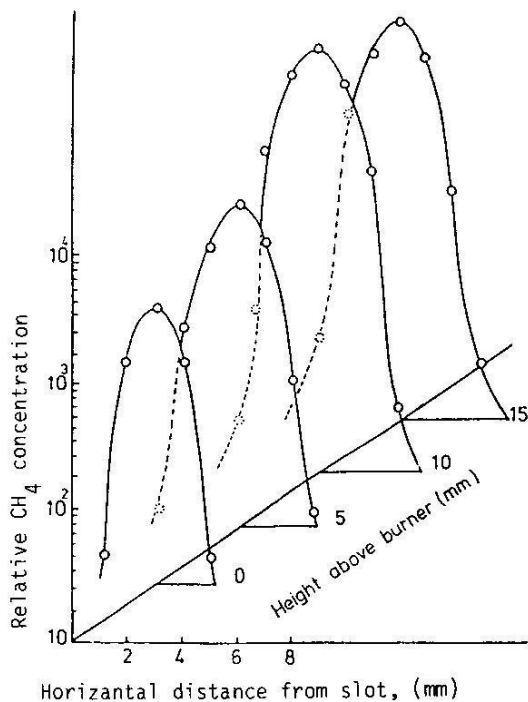


Fig.6: Horizontal distribution of CH_4 in flame at different heights.

Butanone aspirated: 25% Hyd/Air ratio: 1.5.

flame are shown in Fig.7. Unlike the hydrocarbons the maximum concentration of ketones was not associated with any specific region in the flame but was found just above the burner slot, gradually diminishing in the higher regions of the flame. However the maximum concentration of methanol and formaldehyde was observed a little higher above the slot.

An increase in the hydrogen content of the flame affected the concentrations of these species significantly. It reduced the concentration of butanone and made the concentration fall relatively more sharply whereas methanol content was increased and the region of its maximum concentration was also pushed higher up in the flame. Formaldehyde concentration was

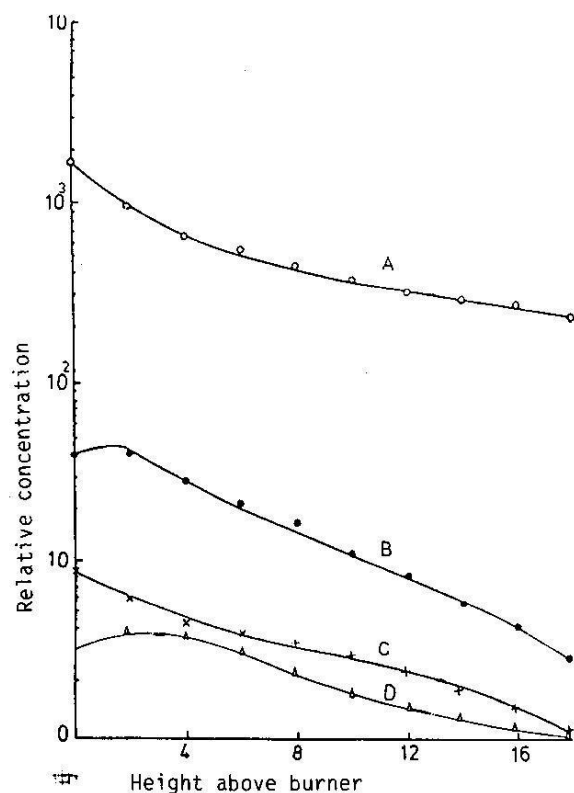


Fig.7: Variation in the concentrations of butanone, acetone, methanol and formaldehyde. Butanone aspirated: 25%, Hyd/Air ratio: 1.5 A-butane, B-methanol, C-acetone D-formaldehyde.

slightly reduced by increasing the hydrogen flow in the flame.

This suggests that the presence of methanol in flame gases was due to the combination of hydroxyl radicals and methyl radicals which resulted from the fragmentation of the butanone. The presence of formaldehyde in hydrocarbon flames is well known and its spectrum has been fully investigated [9]. This compound is probably formed by the combination of one of the fragmentation products of the butanone with hydrogen or hydroxyl radical. The two possible reactions for its formation may be



The probability of reaction I is greater because the concentration of formaldehyde decreases with the increase of hydrogen content in the flame. The second conclusion which can be drawn from this part of the work is that formaldehyde either reacts to give some other species in the flame or is oxidized to formic acid as its concentration decreases higher up in the flame. The literature reveals that absorption bands of formic acid have been observed during the combustion of organic solvents [10].

The presence of acetone, however, was most unexpected and unlikely. The only possible explanation which may be provided in this case is that acetone was present as an impurity in the butanone which was confirmed when the original butanone was sampled on gas chromatograph.

Oxides of Carbon:

As the molecular sieve column used for studying carbon monoxide offered a late and broad signal for carbon dioxide, a silica gel column was used for the latter, which separated it more efficiently.

Fig.8 and 9 show variation in concentrations of carbon oxides with height above burner at different hydrogen flow-rates. The concentrations of both gases in different parts of the lean flame were markedly different from each other. In this flame the maximum carbon monoxide level was found within 5 mm above the burner, then its concentration slowly decreased in the rest of the flame whereas relatively little carbon dioxide was present in the lower part of the lean

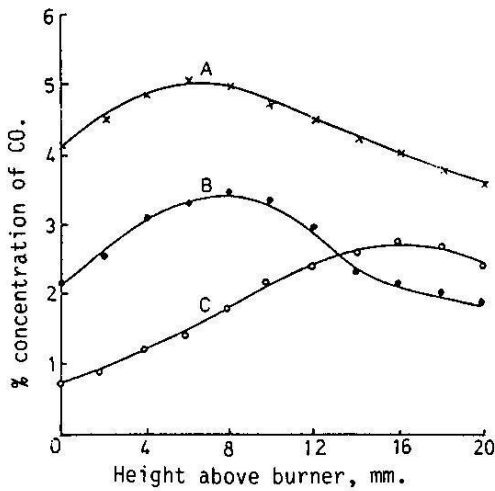


Fig.8: Variation in CO concentration with height above burner. Butanone aspirated : 25%, Hyd/Air: A-1, B-1.5, C-2.

flame and the level gradually increased to a maximum in the higher regions of the flame. This suggests that carbon monoxide might be produced as a direct result of pyrolysis of the organic solvent while carbon dioxide

is formed in the higher regions probably due to the oxidation of carbon monoxide and other relevant species.

In the medium flame, with a 2 mm blue cone, the maximum concentration of both oxides was found just above the blue combustion zone. As the figures illustrate there was a slight decrease in concentrations of both oxides after crossing the edge of the blue cone and then there was a mild enhancement of the concentration of carbon dioxide when carbon monoxide continuing to decrease. The maximum concentration of both oxides just above the blue cone reflects the combustion and oxidation of organic radicals within the cone. The increase in carbon dioxide concentration even above the cone can be attributed to the conversion of carbon monoxide into dioxide.

In a fuel-rich flame the production of both oxides was very slow and took place well high in the flame. An important conclusion which can be

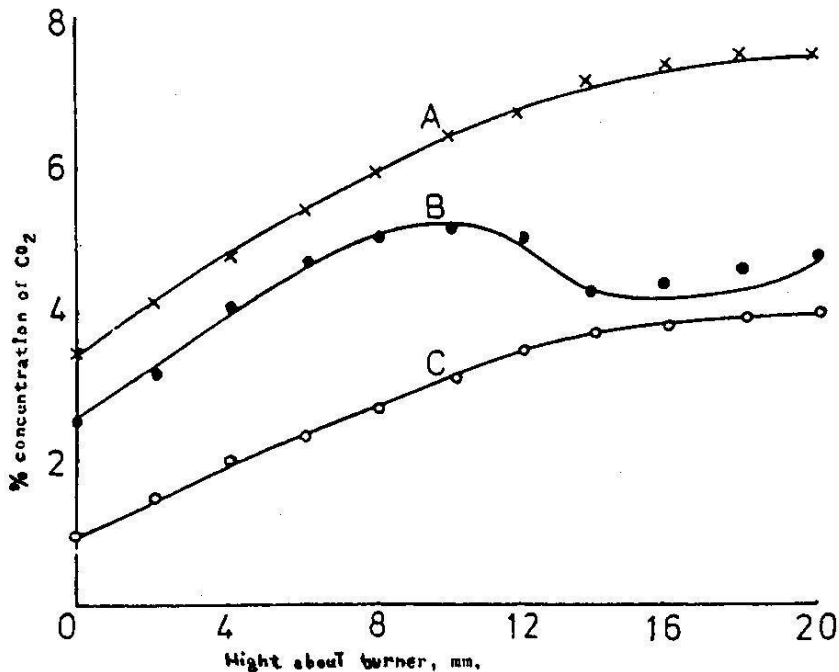


Fig.9: Variation in CO₂ concentration with height above burner. Conditions as for Fig.8.

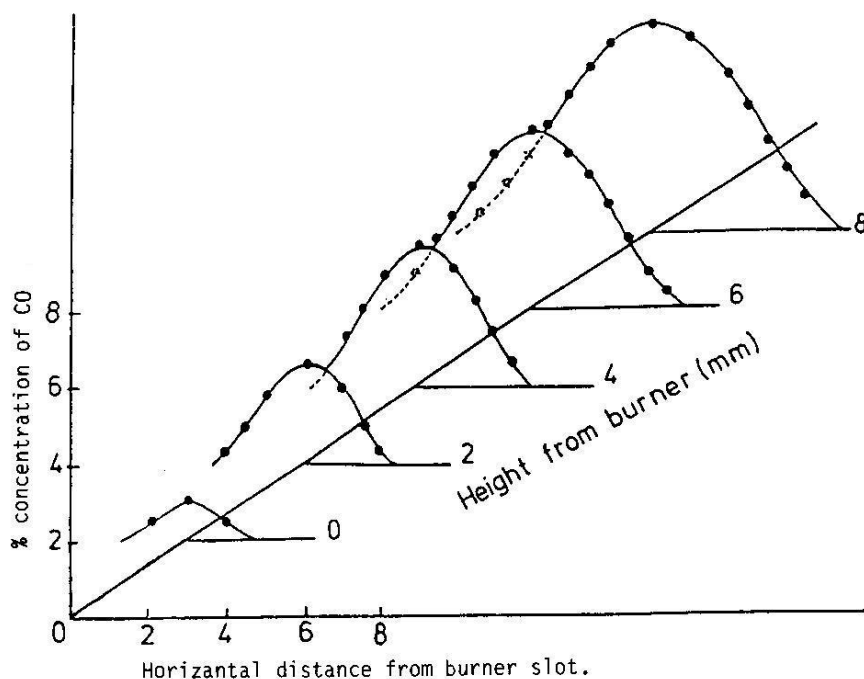


Fig.10: Horizontal distribution of CO in flame at different heights. Conditions as for Fig.4.

drawn from this observation is that concentrations of both carbon oxides in the flame depended inversely on the hydrogen content of the flame.

The variation in the concentrations of carbon oxides along the horizontal axis of the flame at different heights has also been studied. Fig.10 reflects the horizontal profiles of carbon monoxide. As compared to hydrocarbons, the decrease in carbon oxides along this axis is significantly less sharp. This reflects that outer mantle of the flame contains higher levels of carbon oxides rather than hydrocarbons, as air is entrained and assists in completing the combustion.

Hydrogen, Oxygen and Nitrogen:

Though these gases could easily be detected, their relative concentrations could not be monitored as these

were present in large excess in and around flame. Hence in this part of work no valuable information could be obtained for any of the flame condition except the conclusion that the percentage of hydrogen in flame gases increased parallel to the hydrogen ratio as a fuel gas in the flame.

The Conclusion:

Present work was the last part of the investigations related to the effect of organic solvents on the atomic absorption of tin in air-hydrogen flames. In this section we shall try to explain these unusual effects on the basis of the evidence obtained throughout the studies.

Our studies confirmed the fact that in the presence of organic solvents, tin absorption is severely depressed in a fuel-rich air-hydrogen

Table-1: Detail of Instrumental Conditions

Instrument	Column & Conditions	Species	Retention Time (min)
Perkin Elmer F ₃₃ Gas Chromatograph with Perkin Elmer Chart recorder	Column: Activated Alumina	CH	0.7
	Oven temp: 120°C	C ₂ H ₆	1.5
	Carrier gas: N ₂ 20 Psig	C ₂ H ₄	2.2
	Detector: FID	C ₃ H ₈	5.4
	H ₂ /air for detector:20/20	C ₃ H ₆	10.5
-do-	Column: Chromosorb 101	C ₂ H ₂	18.0
	Oven temp: 170°C	CH ₃ OH	4.2
	Carrier gas: N ₂ 8 Psig	C ₂ H ₅ OH	5.4
	Detector: FID	Acetone	6.6
Philips PU4000 gas Chromatograph with Servoscribe chart recorder.	Column: Molecular Sieve	Butanone	11.2
	Oven temp: 30°C	H ₂	0.5
	Carrier gas: Ar 20 Psig	O ₂	1.0
	Detector: TCD	N ₂	1.7
		CH ₄	3.7
Lab-made gas Chromatograph with Servoscribe chart recorder.	Column: Silica gel	CO	7.2
	Oven temp: 50°C	CO ₂	2.0
	Carrier gas: He 20 Psig		
	Detector: TCD		

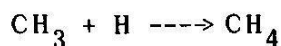
All columns were 2mx3mm stainless steel.

flame which is otherwise an ideal flame for the purpose. This depression can not be attributed to any physical or thermal phenomenon. A number of workers believe that high absorption sensitivity of tin in cool hydrogen flames is a result of chemical atomization in which hydrogen radicals play a vital role [11-13].

The substantial and almost parallel depression in the emission of HPO and CuH to that of the tin absorption, found in present work reveals that

hydrogen radicals are very much involved in tin atomization [8]. A close and inverse relationship found between absorption by methyl radicals and by tin also provides an important and valuable information. It seems that in presence of organic solvents, radicals produced by the pyrolysis of the solvent molecules react with dissociated hydrogen atoms and result in depletion of the active hydrogen in certain regions of the flame. The significant amount of methane present in the combustion zone of the flame is a clear

indication of the reaction between methyl radicals and hydrogen atoms:



There may be a number of other such reactions which involve the hydrogen atoms and organic radicals. The depletion of active hydrogen atoms adversely affects the interaction between hydrogen atoms and the molecular tin-containing species and consequently a depression occurs in tin atomization.

As far as the flame geometry and height in the flame is concerned these factors have a general effect on the elements whose absorption does not depend on any chemical reaction in the flame but the region of measurement becomes more important whenever absorption does depend upon chemical atomization and the chemical atomization takes place in a particular region. In the case of tin, in aqueous solutions maximum absorption occurs very close to the burner slot. On the other hand 99% of the hydrocarbon content has been found inside the blue cone above the slot which indicates that most of the recombination reactions occur inside the cone.

In lean flames the radical recombination reactions occur low in the flame, below the part where the tin absorption is being measured. There is then no apparent interference in the determination of tin rather an improvement in sensitivity due to increased nebulization is observed. On the other hand in fuel-rich flames when the blue combustion zone extends to and overlaps the part of the flame

where tin atoms are being produced by the interaction between hydrogen atoms and molecular tin species and are then being observed by atomic absorption measurements, significant depression of the tin signal is to be expected.

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