

Effects of Dopants on Tin Emission in a Helium Microwave-induced Plasma

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Tin is prone to form refractory oxides in a microwave-induced plasma environment in the presence of oxygen. In order to minimise the formation and deposition processes, various dopants were evaluated. From these, sulphur hexafluoride (SF_6) gave the best results. It minimised tin oxide deposition thus leading to a better sensitivity for tin. Analytical performances for the determination of organotin compounds are also given.

Keywords: Tin; microwave-induced plasma; oxide formation; dopant

Since its introduction in 1965^{1,2} as a chromatographic detector, the microwave-induced plasma (MIP) has been widely used as an atomisation and excitation source for atomic emission spectrometry (AES). The MIPs are relatively inexpensive to operate and can excite a large number of elements, including non-metals. The importance of MIPs in analytical chemistry has been documented in several reviews.³⁻⁶ Numerous types of microwave cavity structures exist⁷ and despite its limitations, the most popular is still the TM_{010} Beenakker resonant cavity.⁸ As an alternative, a surface wave launching device called the surfatron has been developed⁹ and used to generate and sustain plasmas of various gases, including those of nitrogen and xenon.¹⁰ The plasmas produced by the surfatron are extremely stable over wide ranges of gas flow-rates, pressures and operating powers. Moreover, tuning is easily carried out and remains constant. Recent applications to spectrochemical analysis have been achieved successfully.¹¹⁻¹³

Microwave-induced plasmas are usually operated at low power (<200 W), and thus the analytical results obtained for liquid samples are fairly limited. Therefore, the use of MIPs is most relevant for the analysis of gaseous samples and consequently, they are widely used as detectors in gas chromatography. Nonetheless, a persistent problem with MIPs is that of material deposition on the discharge tube walls. The deposits are particularly noticeable for long-chain hydrocarbons and other oxygen-free compounds. This problem is even more acute with samples containing inorganic compounds prone to forming refractory species.

Under those circumstances, refractory material depositions are observed on the inner wall of the discharge tube.¹⁴⁻²⁰ In the instance where these are carbon and sulphur deposits, they can be removed by introducing trace amounts of molecular oxygen (scavenger gas) at a concentration not exceeding 2.5% V/V.¹⁴ Nitrogen can also be used as a scavenger gas for carbon¹⁵⁻¹⁷ and phosphorus¹⁸ deposits. However, the removal of these deposits implies the formation of volatile species of the elements. The addition of hydrogen to the helium discharge had no effect on chromium emission^{19,20} but had an adverse effect on the main group non-metals and a majority of transition metals. These effects were mitigated for boron, aluminium, germanium, tin, lead and phosphorus and the response was improved by a factor of 2-3 when the helium discharge was doped with 0.28-0.56% V/V hydrogen.²⁰ This occurs because hydrogen prevents the formation of refractory oxides by binding the free oxygen to form a hydroxy radical. As a drawback, hydrogen quenches microwave energy thus reducing the over-all excitation energy of the plasma, therefore, the ionic emission line intensities are reduced.

In this study, the effects of doping compounds on the emission intensity of tin in an MIP were investigated. As tin is

prone to form refractory oxides, an attempt was made to minimise this problem. The effects of various dopants were examined and the analytical performances for the determination of tin are given.

Experimental

Chemicals

Benzene, carbon tetrachloride, 1,1,2-trichlorotrifluoroethane (Freon 113), chlorotrimethyltin, tin(IV) chloride pentahydrate, tetramethyltin and *n*-butyl magnesium chloride, were obtained from Aldrich Chemicals, (Milwaukee, WI, USA). Dichlorodimethyltin and trichloromethyltin were obtained from Alfa Products, Ventron, (Danvers, MA, USA). Argon, helium, sulphur hexafluoride, gas mixtures of oxygen 0.98% V/V in helium and hydrogen 0.52% V/V in helium were obtained from Cryo-Gaz (Montréal, Canada). All these gases were of commercial-grade purity and were purified by flowing through a trap containing 0.5-nm molecular sieves. A mixture of Me_3SnBu - Me_2SnBu_2 - MeSnBu_3 and SnBu_4 in benzene was prepared after butylation of the chlorinated salts of methyltin, following the method previously described by Chau *et al.*²¹

System Description

Equipment for plasma generation

Two microwave generators are used in our experiments. A Microtron 200 Mark III (Electromedicals Supplies, Oxfordshire, UK) operated at 2.45 GHz (0-200 W) is used for the chromatographic work. For the optimisation work, the power is supplied by a Kiva MPG4 (Rockville, MD, USA) operated at 2.45 GHz, (0-120 W). The power calibration is performed before use, following the procedure described by Hubert *et al.*²² Short (50 cm) co-axial cables (RG-214 U/50 μ) are used in order to prevent power leakage by radiation.

The atmospheric-pressure helium MIP is generated by a surfatron.¹² The plasma produced by this device is sustained in a discharge tube obtained by joining a 6 mm o.d., 3 mm i.d. quartz tube to a 6 mm o.d., 1 mm i.d. quartz tube.¹³ The plasma discharge is located inside the tube with the largest i.d. a few millimetres from the junction of the two tubes. Improved signal to noise ratios were obtained for a large number of elements including tin with this particular type of discharge tube. The plasma can be observed both axially or transversally. Owing to etching and various deposition processes, the tube gradually loses its transparency and thus axial viewing is preferred. To prevent overheating of the structure and discharge tube, compressed air is circulated through the surfatron.

Optical system

Two monochromators are used for this experiment. The chromatographic work requires a Spex 1800-II spectrometer

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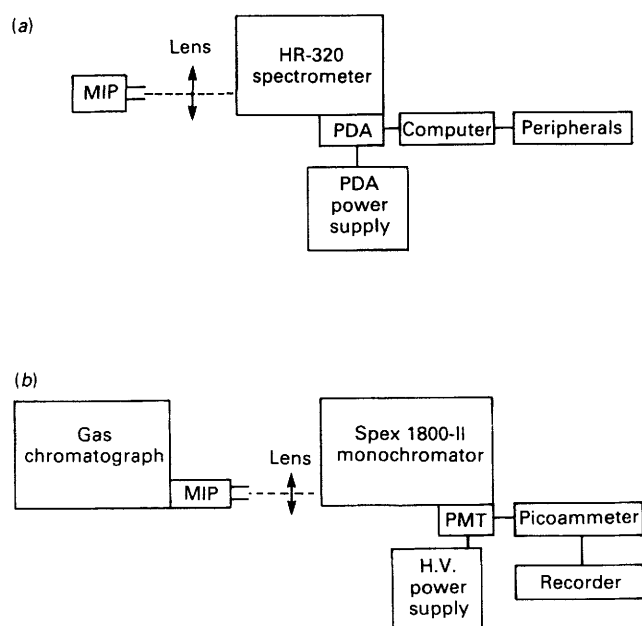


Fig. 1. Block diagrams of the experimental arrangement: (a) optimisation and (b) chromatographic arrangements

(Metuchen, NJ, USA) with a focal length of 0.75 m. It has a grating, ruled with 1200 grooves mm^{-1} blazed at 500 nm. The tin response is monitored at 284.00 nm with a monochromator slit that is 0.05 mm in width. The intensity is measured with a Hamamatsu R636 photomultiplier (Hamamatsu, Japan) operated at -1000 V; a Keithley 414S picoammeter was used to measure the photocurrent (Cleveland, OH, USA). For the optimisation work, a Jobin-Yvon HR-320 monochromator (Longjumeau, France) with a focal length of 0.32 m and equipped with a Reticon RL-1024S photodiode array (Sunnyvale, CA, USA) is used. This allows the simultaneous observation of a spectral region 62 nm wide with a holographic grating ruled with 1200 grooves mm^{-1} optimised in the UV. Block diagrams of the systems used in this work are shown in Fig. 1(a) and (b).

Sample introduction

A Hewlett-Packard 5751A (Avondale, CA, USA) gas chromatograph is used. The packed column is $1.8 \text{ m} \times 2 \text{ mm i.d.}$, packed with 5% SE-30 on 80-100 Chromosorb W-HP. A heated brass block is used as an interface between the surfatron and the gas chromatograph. In order to prevent condensation, this block is heated to 250°C . A valve at the end of the column allows the venting of column effluent containing large amounts of solvent which would otherwise cause excessive carbon deposits and plasma disruption. In addition to the gas chromatograph, another sample introduction method is used to allow a constant introduction of small amounts of various compounds. It consists of a thermostated diffusion capillary (length 5 cm, 1-mm i.d.) filled with a volatile liquid and connected by a T-joint to the carrier-gas line.

Procedure

The flow-rate was kept constant at 500 ml min^{-1} and the power set at 90 W. These are the optimum values for tin atomic emission. The spectrum obtained when tetramethyltin is introduced into the MIP is considered as the reference spectrum. With the volatile organotin compound continuously swept into the plasma, dopants are introduced and the resulting spectra are recorded. The evaluation of the effect of each dopant is made by comparing the tin response with and without dopants.

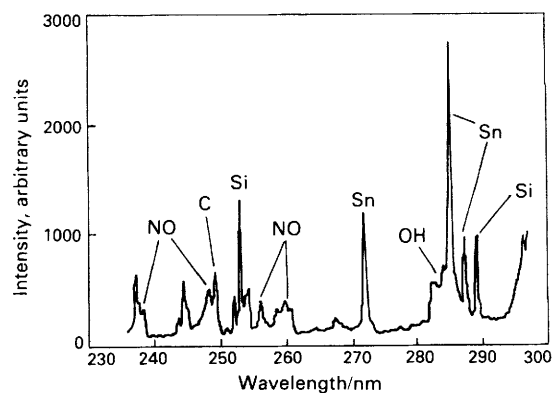


Fig. 2. Me_4Sn doped helium plasma emission spectrum in the 235–295 nm region; forward power, 90 W

In order to ascertain the effect of the dopants on the chromatographic peaks of organotin compounds, a benzene solution of methylbutyltin compounds ($\text{Me}_n\text{SnBu}_{4-n}$ for $n = 0-3$) is injected ($0.5 \mu\text{l}$) into the chromatograph. The peaks are well resolved with temperature programming. The initial temperature is set at 70°C for 2 min, then increased to 220°C at a rate of $20^\circ\text{C min}^{-1}$ and allowed to stand for 1 min at this maximum temperature. A comparison is made of the chromatograms obtained with and without dopant by studying the heights and tailings of the peaks.

Results and Discussion

MIP Emission

The atmospheric pressure of a Me_4Sn -doped helium-plasma emission spectrum gives the molecular emission bands of NO and OH and the atomic emission lines of tin, silicon and carbon in the 235–295-nm region (Fig. 2). There are three potential sources for the background spectral emissions observed. The first is related to the impurities present in the plasma gas (O_2 , N_2 , H_2 , C, hydrocarbon and carbon oxides) and the second is related to the impurities released into plasma by etching of the quartz tube (Si and O). The third source is attributed to the back-diffusion of air into the plasma (N_2 and O_2). To decrease the residual concentration of impurities in the plasma gas, the helium was circulated through a trap of liquid nitrogen. A decrease of up to 40% of the N_2 and NH molecular emissions was observed, but no significant effect was noticed on the OH and C emissions. Increasing the pressure of the gas in the cold trap from 40 to 160 lb in^{-2} decreased the OH emission slightly, but no change was observed for the other molecular emissions. The optimum flow-rates for carbon and tin were investigated by monitoring their emissions at 247.86 (C I) and 284.00 nm (Sn I), respectively (Fig. 3). Their optimum flow-rates were determined to be 100 and 500 ml min^{-1} , respectively. The observed carbon-emission intensity change with flow-rate was typical of non-metallic elements, while that obtained for tin exhibited the behaviour expected of metals.

For carbon and tin, the decreasing part of the curves can be explained by a lower residence time which leads to a reduction of atomisation and/or excitation. For tin, the ascending part (below 500 ml min^{-1} , Fig. 3) of the curve can be explained in several ways. We have observed that the molecular emissions tend to drop when the flow-rate is increased to 500 ml min^{-1} . At low flow-rates, the larger amounts of molecular species in the plasma affect the excitation of carbon and tin by either quenching the active plasma species (electrons, metastables and ions) or by forming molecular species such as SnH , SnO , SnOH , CO or CN with tin and carbon. If we assume that the most important molecular species formed are the oxides and as tin oxide is a refractory compound and carbon oxides are volatile, a difference in behaviour can be expected. At low

flow-rates only a small fraction of tin oxide is atomised and excited.

Increasing the flow-rate decreases the concentration of species other than the analyte and the impurities originally present in the plasma gas. Indeed, a higher flow-rate will cool the discharge tube more efficiently, thus reducing the release of species from the quartz and decreasing the back-diffusion of air. Thus the nitrogen and oxygen concentrations in the plasma will be reduced. A decrease of the species, other than the analyte in the plasma, leads to weaker competition for the microwave energy and provides better atomisation and excitation conditions for the analyte.

Tin Oxide Deposits Control

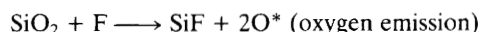
During this work, tin oxide deposits were noticed, particularly when Me_4Sn was continuously swept into the plasma, but also after repeated injections into the gas chromatograph. These deposits were positioned within a millimetre of the discharge either upstream or downstream. Plasma fluctuations caused a re-introduction of these deposits into the discharge and led to atomisation, excitation and temporally non-specific emission, particularly in the chromatographic mode.

In order to minimise the formation of tin oxides, we doped the helium plasma with liquids or gaseous dopants. We noticed that the presence of water vapour in the plasma gas increased the intensity of tin emission. To determine which of the constituents, hydrogen or oxygen, was responsible for this effect, we successively doped the helium with a maximum concentration of 0.52% V/V hydrogen and 0.98% V/V oxygen. When a new discharge tube was used and the hydrogen concentration was varied from 0 to 0.52% V/V, the tin emission decreased by 50%. The NO molecular emission

disappeared totally while the OH emission increased. However, the opposite effect for the tin emission can be observed when the discharge tube is used for some time. Therefore, the effect of H_2 is difficult to evaluate. It is a function of the discharge tube condition and opposite results can be obtained. Estes *et al.*²⁰ recently reported that in a hydrogen-doped helium plasma (0.28–0.56% V/V) the tin emission intensity was doubled. Estes *et al.* explained this effect by the trapping of free oxygen and preferential formation of the hydroxy group, OH. In our work, the OH emission intensity increased but the tin response decreased constantly. This can be attributed to the fact that hydrogen quenches the available microwave excitation energy. The addition of oxygen induces a decrease in intensity of all the emission lines between 235 and 295 nm. Consequently, the observed effect of water may be attributed to the cooling of the quartz tube, which is in agreement with the fact that the emission lines of silicon (251.6 and 288.1 nm) are suppressed by 80% during water vapour entrainment. This observation reinforces the hypothesis that water has a cooling effect on the quartz wall and decreases the release of oxygen from the discharge-tube wall.

Another approach used to minimise the problems associated with tin oxide formation involved the formation of a volatile halogenated species of tin. We successively doped the helium plasma with CCl_4 and $\text{CCl}_2\text{FCF}_2\text{Cl}$ (Freon 113) in order to evaluate the effect of chlorine and fluorine. The use of F_2 or Cl_2 is also possible but these gases require special handling. The resulting spectra are reproduced in Fig. 4. As a point of reference, the spectrum obtained with the constant introduction of Me_4Sn into the helium plasma is also reproduced in Fig. 4(a). The introduction of CCl_4 into the discharge [Fig. 4(b)] increases the emission intensities of silicon and tin while the OH emission is not affected. Formation of atomic chlorine, following CCl_4 atomisation, tends to increase the quartz etching and allows the re-introduction of silicon and tin oxide deposits into the plasma. The effect of Freon 113 [Fig. 4(c)] is similar but more noticeable than for CCl_4 .

A possible reaction scheme for the attack on quartz by fluorine has been proposed⁵:



where O^* and Si^* are the excited states of oxygen and silicon. The effect of the addition of halogens is interesting, as they increase the tin emission while the background emission remains almost unaffected. However, it is not without its shortcomings. First, the halogens accelerate the quartz degradation and second, the doping compounds used also contain carbon. Unfortunately, in an attempt to detect the carbon and tin for the analysis of organotin compounds simultaneously, the use of carbon-containing dopants is not

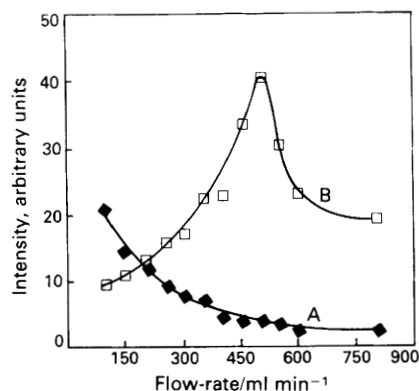


Fig. 3. Effect of helium flow-rate on carbon (A) (247.86 nm) and tin (B) (284.00 nm) emission intensities

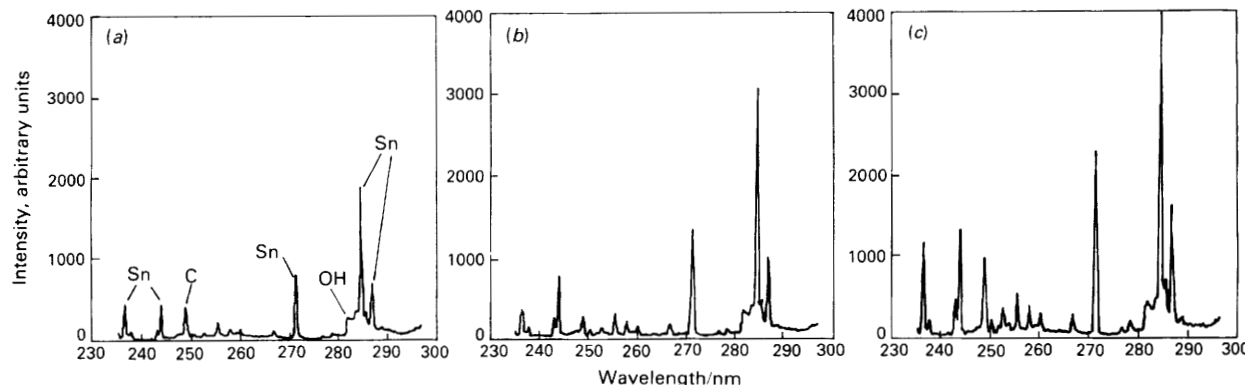


Fig. 4. Effects of halogenated dopants on tin emission intensity: (a) no dopant; (b) CCl_4 ; and (c) Freon 113

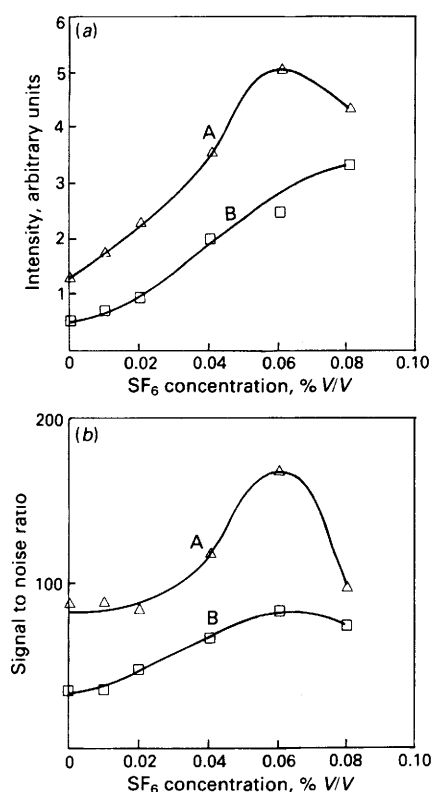


Fig. 5. Effect of the SF_6 concentration on: (a) tin emission intensity and (b) tin signal to noise ratio. A, SnBu_4 ; and B, Me_3SnBu

desirable. To circumvent this problem, we used SF_6 as a dopant. With the introduction of SF_6 , the helium plasma becomes blue and important increases in tin and carbon line emissions were observed. Preliminary studies of this gaseous dopant showed that the concentration should be kept lower than 0.1% V/V to prevent a strong attack on the quartz tube. Organotin peak-tailing has been observed previously²⁰ and may be due to semi-reversible adsorption of these compounds on to the quartz wall or gradual release of tin oxides from the discharge tube.

The concentration of SF_6 was varied between 0 and 0.08% V/V. A mixture of methylbutyltin compounds was injected in order to obtain at least three reproducible results for each concentration level. The emission intensity of Me_3SnBu increased continually with the concentration of SF_6 , while a maximum was attained at 0.06% V/V for SnBu_4 [Fig. 5(a)]. The behaviour of Me_2SnBu_2 and MeSnBu_3 is similar to that of Me_3SnBu thus their curves are not presented. The emission intensities are increased by a factor of 4–8 and a maximum signal to noise ratio is observed [Fig. 5(b)] for each compound at 0.06% V/V SF_6 . At this concentration, the signal to noise ratios are twice as high as those obtained without dopant. At concentrations higher than 0.06% V/V, SF_6 causes a stronger etching of the quartz tube which increases the concentration of the released species in the plasma. This leads to a more prominent background and noise level, causing a drop in the signal to noise ratios.

When SF_6 was used as a dopant, no deposits were observed on the quartz wall. It appears that tin oxide deposits can therefore be controlled by the addition of SF_6 at an optimum concentration of 0.06% V/V. However, the chromatographic peaks of organotin compounds still exhibit tailing. We noticed that the tailing increases as the tube wall becomes more eroded. Further, tailing is more prominent when the tin emission line is monitored instead of the carbon emission line. This suggests that tin still interacts with the quartz, although in a much lower proportion and despite the use of SF_6 .

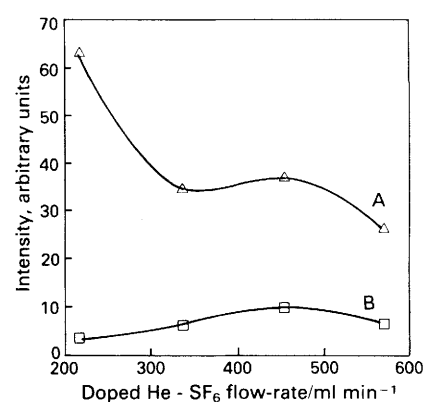


Fig. 6. Effect of doped helium - SF_6 mixture (0.06% V/V) flow-rate on tin emission intensity: A, SnBu_4 ; and B, Me_3SnBu

Table 1. Analytical performances for organotin determination.

Solute	Detection limit*			Selectivity ($\times 10^3$)†	
	pg s^{-1}	pmol s^{-1}	pmol^\ddagger	Mass	Molar
Me_3SnBu	18	0.15	1.2	2.5	25
Me_2SnBu_2	12	0.08	0.6	3.5	39
MeSnBu_3	10	0.08	0.6	4.0	45
SnBu_4	8	0.08	0.6	5.0	55

* The detection limit is defined as three times the standard deviation of the blank signal divided by the sensitivity.

† The selectivity is defined as the peak-area signal of the analyte per mass (g), or moles of analyte divided by the peak-area signal of carbon per mass (g), or moles of carbon at the analyte emission wavelength.

‡ The values are obtained for a chromatographic peak width at a half maximum of 8 s.

If the flow-rate dependency of the tin emission is a function of the tin oxide deposits, and if an effective way to control the tin oxide formation can be achieved by doping the gas with SF_6 , then we can postulate that the behaviour of tin in the helium MIP will be similar to that observed for carbon. In order to verify this, we optimised the 0.06% V/V SF_6 -doped helium flow-rate for the various methylbutyltin compounds (Fig. 6). The results obtained were interesting. For SnBu_4 , the optimum flow-rate was 200 ml min^{-1} , the same tendency was found with MeSnBu_3 and Me_2SnBu_2 . For Me_3SnBu , the optimum flow-rate was 450 ml min^{-1} . These compounds appear to exhibit different behaviours in the plasma and we believe that this is possibly due to the degree of butyl substitution.

Analytical Performances

The differences in the behaviour of the methylbutyltin compounds were also noticed when establishing calibration curves as the greatest sensitivity for tin was observed with SnBu_4 and the lowest with Me_3SnBu . It consequently leads to differences in terms of detection limit, both absolute and relative, to the mass flow-rate of the element entering the plasma and the selectivity. These results, all obtained under the same operating conditions, are listed in Table 1.

The calibration graphs of the methylbutyltin compounds appear to be the same when using a flame ionisation detector, with the exception of SnBu_4 which has the lowest sensitivity regarding carbon. Flame photometric detectors (FPD) present good sensitivities for the butyltin compounds. With a modified FPD, Aue and Flinn²³ reported a limit of detection of $5 \times 10^{-16} \text{ g s}^{-1}$ of tin ($4 \times 10^{-15} \text{ mole s}^{-1}$ of Sn). Under normal conditions, the FPD gives a limit of detection in the same order of magnitude as the MIP. Maguire and Tkacz,²⁴

with a conventional FPD, reported a limit of detection ranging from 60 to 150 pg for butyltin compounds. Our values are lower by a factor of 8.

If we compare our data, with those obtained by other groups working with microwave plasma sources, we find that compared with reference 25, our detection limits are lower by a factor of 3. Only Estes *et al.*²⁰ reported detection limits (1.6 pg s⁻¹ of Sn) that were lower than ours, by a factor ranging from 4 to 9. Their detection limits were calculated for a signal to noise ratio of 2.

Conclusion

The atmospheric pressure helium MIP was doped with various liquids and gaseous dopants. Among them, SF₆ showed the most interesting effects regarding the tin emission response and oxide-formation related problems. The optimum concentration of SF₆ in helium was found to be 0.06% V/V. At this concentration, methylbutyltin compound intensities were improved 4- to 8-fold and signal to noise ratios were at least doubled. The observed SF₆ effect allows us to suggest that the different behaviour of metallic and non-metallic elements in the MIP is largely due to the capacity of the analyte to form refractory oxides.

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