EFFECT OF ORGANOTIN SPECIES ON THE EMISSION SIGNAL IN ICP-AES

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INTRODUCTION

It is generally accepted that the analytical response in ICP-AES is not influenced by the chemical form of the analyte. Nevertheless, differences between signals of organometallic and inorganic compounds of the same analyte have been reported [1,2]. Thus, it has been proved that inorganic tin solutions provide higher emission signals than organotin ones. Moreover, this behaviour has been observed operating with different spray chambers and experimental conditions[3].

The aim of this work is to evaluate the analyte chemical form on the emission signal in ICP-AES. To this end, different tin solutions have been analysed using a pneumatic concentric nebulizer coupled to a cyclonic spray chamber. The effect of the liquid and gas flow rates on the aerosol drop size distribution, solution transport rate and emission signal in ICP-AES have been studied.

REFERENCES:
(1) L.C. Alves, M.G. Minnich, D.R. Wiederin, R.S. Houk, J. Anal. At. Spectrom., 9, 399 (1994).
(2) C. Rivas, L. Ebdon, S.J. Hill, J. Anal. Spectrom., 11, 1147 (1996).
(3) J. Montiel, J. Mora, Influence of the analyte chemical form and the sample introduction system on the analysis of organotin compounds by ICP-AES, Euroanalysis XIII, Salamanca, 2004.

EXPERIMENTAL

- 10 ppm Sn in EtOH 0.75% from: $SnCl_4$; $^{n}BuSnCl_3$ (MBT); $^{n}Bu_2SnCl_2$ (DBT); $^{t}Bu_2SnCl_2$ (DTBT)
- Sample introduction system:

Meinhard ® TR-30-A3 nebulizer

Cyclonic Spray Chamber

- ICP-AES operating conditions:

PERKIN ELMER OPTIMA 4300 DV	
RF Power (W)	1300
Plasma gas flow rate (L/min)	15
Auxiliar gas flow rate (L/min)	0,2
Nebulizer gas flow rate, Q_g, (L/min)	0,6
Liquid flow rate , Q_l, (mL/min)	0,2 - 1,0
i.d. injector (mm)	1,2
Sample and integration time (s)	Automatic
Torch position (mm)	15
Vision view	axial

RESULTS

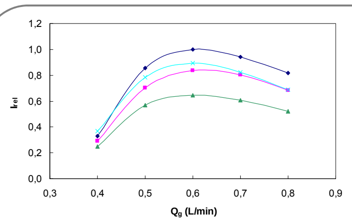


Figure 1. *Effect of Q_g on the relative tin emission signal for the different solutions tested: (—◆—) $SnCl_4$; (—■—) MBT; (—×—) DTBT; (—▲—) DBT. Q_l = 1,0 mL/min. Sn II 283,998 nm*

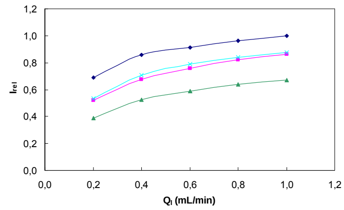
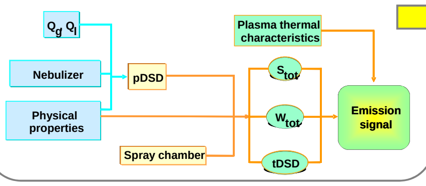


Figure 2. *Effect of Q_l on the relative tin emission signal for the different solutions tested: (—◆—) $SnCl_4$; (—■—) MBT; (—×—) DTBT; (—▲—) DBT. Q_g = 0,6 L/min. Sn II 283,998 nm*

$I_{SnCl_4} > I_{DTBT} \approx I_{MBT} > I_{DBT}$

EMISSION SIGNAL DEPENDS ON THE TIN COMPOUND



- There is no effect of analyte chemical form on:
  - Primary droplet size distribution (pDSD) **(1)**
  - Tertiary droplet size distribution (tDSD) **(2)**
  - Solvent transport rate **(3)**
  - Plasma characteristics **(4)**
- For a given Q_l, the analyte transport rate, W_{tot}, is independent on the analyte and the solution employed.

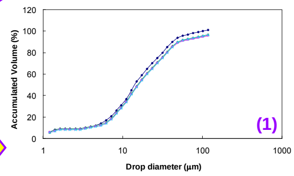


Figure 3. *Primary droplet size distributions for the different solutions tested: (—◆—) $SnCl_4$; (—■—) MBT; (—×—) DTBT; (—▲—) DBT; (—●—) EtOH 0.75 %. Q_g = 0.6 L/min; Q_l = 1.0 mL/min.*

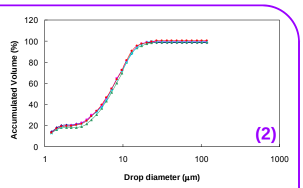


Figure 4. *Tertiary droplet size distributions for the different solutions tested: (—◆—) $SnCl_4$; (—■—) MBT; (—×—) DTBT; (—▲—) DBT; (—●—) EtOH 0.75 %. Q_g = 0,6 L/min; Q_l = 1,0 mL/min.*

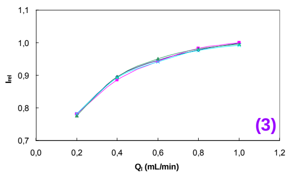


Figure 5. *Effect of Q_l on the relative carbon emission signal for the different solutions tested: (—◆—) $SnCl_4$; (—■—) MBT; (—×—) DTBT; (—▲—) DBT. Q_g = 0,6 L/min. C I 193,030 nm*

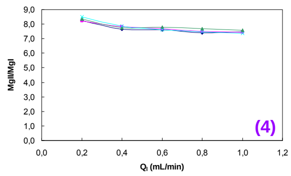


Figure 6. *Effect of Q_l on the magnesium ratio MgII/MgI for the different solutions tested: (—◆—) $SnCl_4$; (—■—) MBT; (—×—) DTBT; (—▲—) DBT. Q_g = 0,6 L/min.*

Q_l (mL/min)	Analyte	W_{tot} (µg/min)				
		Blank*	$SnCl_4$	MBT	DBT	DTBT
0,2	Mg	0,50 ± 0,06	0,57 ± 0,02	0,59 ± 0,05	0,53 ± 0,06	0,56 ± 0,06
0,2	Mn	0,52 ± 0,07	0,54 ± 0,03	0,54 ± 0,05	0,48 ± 0,05	0,52 ± 0,05
1,0	Mg	1,62 ± 0,11	1,67 ± 0,13	1,66 ± 0,11	1,74 ± 0,02	1,9 ± 0,2
1,0	Mn	1,74 ± 0,12	1,63 ± 0,09	1,67 ± 0,05	1,77 ± 0,04	1,8 ± 0,3

* Ethanolic matrix without Sn

COMPOUND VOLATILITY

$W_{tot} = (W)_{\leq d_c} + (W)_{>d_c}$

- ✓ Low volatile analyte ⇨ $W_{tot} \approx (W)_{\leq d_c}$
- ✓ High volatile analyte ⇨ $W_{tot} = (W)_{\leq d_c} + (W)_{>d_c}$

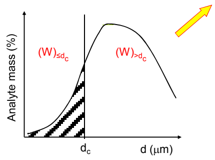


Figure 7. *Analyte mass distribution of the primary aerosol (including a hypothetic value of the cut diameter of the spray chamber, d_c)*

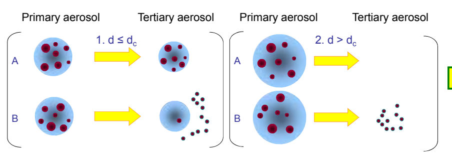


Figure 8. *Effect of analyte volatility and primary aerosol drop size on the tertiary aerosol composition. 1: Analyte initially contained in drops with diameter equal or less to d_c; 2: Analyte initially contained in drops with diameters higher than d_c; A: Low volatile analyte; B: High volatile analyte.*

Compound	Boiling Point (ºC)
$MgCl_2$	1410
$MnCl_2$	2160
$SnCl_4$	110
DTBT*	210
MBT*	240
DBT*	300

* Estimated values (T-H-E rule).

$(W_{tot})_{SnCl_4} > (W_{tot})_{DTBT} \approx (W_{tot})_{MBT} > (W_{tot})_{DBT}$

⇕

$I_{SnCl_4} > I_{DTBT} \approx I_{MBT} > I_{DBT}$

THE HIGHER COMPOUND VOLATILITY THE HIGHER EMISSION SIGNAL IN ICP-AES