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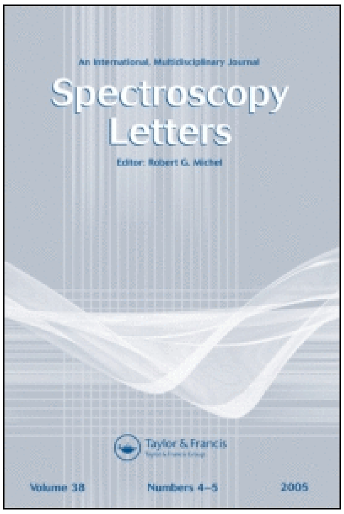

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DELAYED ATOMIZATION FURNACES FOR ELECTROSTATIC SAMPLING OF ATMOSPHERIC PARTICULATES

KEY WORDS: Electrothermal atomization, Airborne lead, Electrostatic precipitation

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ABSTRACT

Graphite furnaces were designed to meet both the requirements of electrostatic sampling of aerosols and of delayed atomization of the sample. The metal lining of the inner surface improves the sensitivity. The carbide coating has no effect when the sample is handled as solid air particulates. High performances were obtained for the atomization of lead in different synthetic and natural matrices; better recoveries were obtained when the sample is directly atomized without chemical pretreatment.

INTRODUCTION

It is highly probable that the endeavour of Torsi et al.[1-4] already resuscitated the interest for the very

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promising technique of electrostatic precipitation of air particulates directly into the electrothermal atomizer[5-7].

However all the disadvantages that plague non-isothermal atomizers, i.e. convectional removal of solid sample fragments; vaporization of the sample into a cooler and "hostile" environment; occurrence of interfering chemical reactions in the gas phase; premature evacuation of the atom cloud will be experienced altogether if the aerosol is sampled on any of the commercial available electrothermal (ET) atomizers.

As such we found it necessary to design atomizer furnaces meant to be used not only for electrostatic precipitation but also for quasiisothermal operation. The design aimed to:

a. efficiently collect the aerosol particles with the highest environmental significance[8],

b. obtain a sample deposit with a symmetry that matches the dry deposit left behind by the evaporating drop of a standard solution[9],

c. delay the sample vaporization until the atmosphere inside the furnace is near the thermal equilibrium with the furnace walls[10].

When the electrostatic microfilter operates according to a point-to-plane (needle-cup) geometry of the corona discharge, the Circular L'vov Platform[9] (CLP) or the Sampling Cup Tube Atomizer[9] (SCTA) were used as collecting electrodes. For the wire-in-tube type of electrostatic microfilter[9] the Coaxial Tube Atomizer (CTA) or its tantalum lined alternative (TaCTA) were used as collecting electrodes.

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The atomization characteristics of these tubes are evaluated in the following with reference to lead as analyte.

EXPERIMENTAL

Circular L'vov Platform CLP (Fig.1-a) is essentially a tiny disk machined from Ringsdorff RWO grade graphite. The dimensions (6.8 mm I.D., 7.5 mm O.D., and 2 mm deep) are a compromise between high collecting area and the risk of beam obstru$\overset{c}{a}$tion when the CLP is placed into the graphite tube (Pye Unicam SP 9-01 standard tube). The CLP is moved in and out of the electrostatic microfilter or the graphite furnace by means of a tantalum cradle.

Early experiments were done with a "boat" shaped L'vov Platform (Fig.1-b). This boat was obtained by removing the excess material from an Instrumentation Laboratory microsampling boat. No significant differences were apparent in the atomization patterns of this platform or with the CLP. However, for electrostatic sampling the CLP was prefered for corona field and sample deposit symmetry reasons.

Sample Cup Tube Atomizer. SCTA is the adaptation for electrostatic sampling of an atomizer earlier described for emission work[11]. SCTA was obtained by cementing the bottom of a Varian Cup in the body of a Pye Unicam SP 9-01 standard tube. (Fig.1-c). Both the cup excavation and the tube hole were enlarged with a 4.5 mm drill to accomodate the corona needle and nozzle assembly. During the sampling the corona assembly protrudes the cup which act as a collecting counterelectrode. A layer of pyrolitic graphite primarily aimed at cementing the cup into its place was deposited on the SCTA by pyrolizing a mixture of 1% acetylene in argon.

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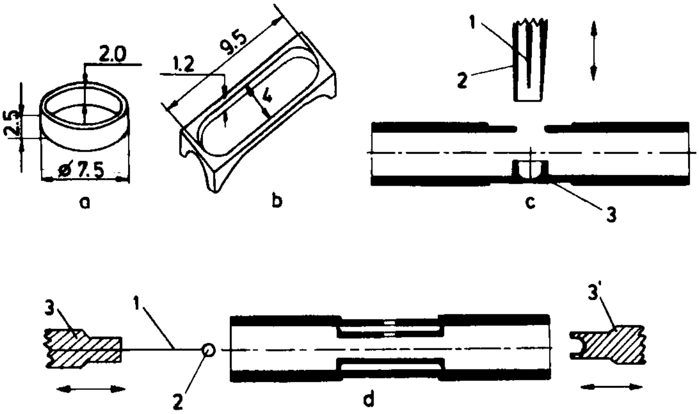

Fig.1. Delayed atomization furnaces. a - circular L'vov platform; b - boat shaped L'vov platform; c - sample cup tube atomizer (1 - corona needle; 2 - corona nozzle); d - coaxially tube atomizer (1 - corona wire; 2 - end bead insulator; 3-guides)

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Coaxial Tube Atomizer. CTA (Fig.1-d) is easy constructed by introducing a smaller graphite tube (6.5 mm I.D., 7.0 mm O.D., and 14 mm long) in the standard graphite tube (8.5 mm I.D.) of a Pye Unicam SP 9-01 electrothermal atomizer. The inner tube is coaxially positioned by means of two end disks and then cemented to the main (outer) tube by pyrolising a mixture of 1% acetylene in argon.

The conductive heating of the inner tube is limited to a minimum by machining the edges of the end disks to have a minimum contact area with the main tube.

The CTA somewhat resembles an earlier described furnace[12] used in conjunction with a Zeeman AA spectrometer or with a recently reported double-walled furnace[13]. During the aerosol sampling sequence the corona wire-guide protrudes the CTA and the inner tube plays the rôle of a collecting electrode.

The TaCTA is essentially the same CTA but the inner tube was lined with a rolled foil of tantalum (Goodfellow Metals, Cambridge, England, TA000360 foil, 0.05 mm thick).

Some of the platforms and tubes were coated with TaC by soaking in TaF_4 according to Zatka's procedure[14]. However no significant differences in the atomization of lead were noticed as long as the sample is handled as a suspension of solid particles[15].

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Atomic Absorption Equipment. The various furnace designs were all used in conjunction with a Pye Unicam SP 9-01 Digital Flameless Atomizer. The development of absorbance signals was monitored with a Pye Unicam SP 2900 AA spectrometer (20 ms theoretical response time) and equipped with a 250 ms f.s.d. Pye Unicam AR 55 recorder) or with an Instrumentation Laboratory 551 Video AA spectrometer (62.5 ms response time and 100 ms f.s.d. CRT display).

Unless otherwise stated, the following experimental conditions were used:

- analyte: Pb, 4 ng, pipetted as $Pb(NO_3)_2$ in aqueous solution,
- wavelength: 283.3 nm, HCL current 5 mA, D_2 arc background correction,
- purge gas flow rate 1.5 l/min argon.

RESULTS AND DISCUSSION

It was expected that the use ot a smaller crossection of the atomizer graphite tube would result in a higher sensitivity.Sensitivity figures obtained with CTA are indeed higher than those with the standard SP 9-01 tube. (Fig. 2) However such reasons cannot be held responsible for the signal enhancement observed in TaCTA tubes.

A faster heating rate of the metal foil is also highly improbable. When ordinary graphite tubes are lined with metal foils and some electrical contact between the foil and the tube walls is expected, it is possible that part of the electrical current flows through the metal foil and contributes to the heating of the foil by the thermoelectric effect. With TaCTA the electrical current can cross only at the edges of the end disks and the contact between the foil and the tube is far from perfect, therefore the contribution of thermoelectric heating of the foil, if any, should be definitely nonsignificant.

The temperature figures on the abscissa (Fig.2) are not the true temperatures but rather the values corresponding to the instrumental setting on the SP 9-01 power supply obtained from the manufacturer's calibration curve for the standard tube. The temperature of the inner tube lags behind that of the outer tube and, because of the higher CTA mass, it is probably lower than the expected value although the heating is voltage controlled. However, since for the same temperature settings the absorbance obtained with the TaCTA is on the decreasing slope while with the CTA is still on the rising slope (Fig.2), there is good agreement with the L'vov's and Pelieva's finding that lower atomization temperature occur on tantalum surfaces.[16]

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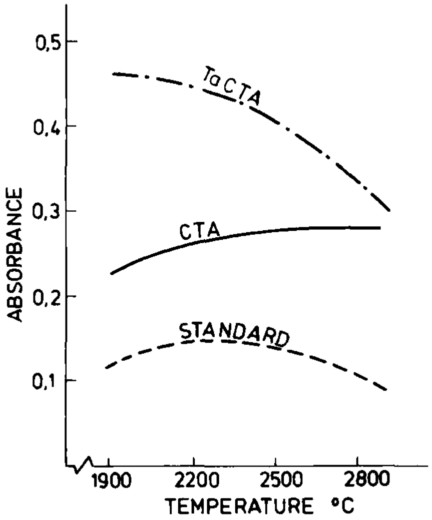

Fig.2. Dependence of the atomization peak height of 4 ng Pb on the atomization temperature.

The lower relative sensitivity improvements obtained by us (lined/unlined tubes) as against the values obtained in the above mentioned work by L'vov and Pelieva can be expplained by heat transfer processes and by the assumption that a significant contribution is brought by convection to the global heat transfer. In an ordinary graphite tube lined with a metal foil the higher thermal conductivity of the metal surface is manifest in a faster heat transfer to both the sample and the sheath gas. In a delayed heating atomizer the sample vaporization takes place when the inner (lined or not) tube becomes heated and at that time the inert gas atmosphere is already hot. Consequently, if the fast heat transfer property of the metal surface is manifest, it can act on the sample deposit only at the

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contact surface and it has a lesser contribution to the vaporization of the rest of the sample because this process is also influenced by the already hot atmosphere. Therefore, in a delayed atomization furnace the entire process of atomization is speeded up to a relatively lesser degree by the metal lining.

Although better sensitivities are associated with, and also it would be a very convenient procedure to collect air particulates on a metal foil and then insert it into the already mounted graphite furnace, unfortunately the aerosol sampling and atomization on a Ta foil cannot be used on a routinely basis. The foil becomes rapidly distorted and nonreproducibly obstructs the optical beam.

The evaluation of the figures of merit of the described atomization furnaces (CLP, CTA, and SCTA) was done by investigating the effect produced by NaCl on the atomization of lead and by determining the recovery of lead in natural aerosol matrices.

The interferences induced by the alcaline halides were emphasized in numerous works[13,17-21]. Clearly, irrespective of the proposed mechanism, the halide presence alters the temporal parameters of the atomization peak. The study of such processes requires a fast response instrumentation[17]. However, we believe that some of the effects of interfering halides on the atomization peak of lead can be elucidated even with commercial equipment. Even though the absolute time resolution of the detection system is far from the ideal, we feel that being given the relatively slow furnace heating rates determines a relative time resolution appropriate to our purpose. Figures 3, a-f, were obtained

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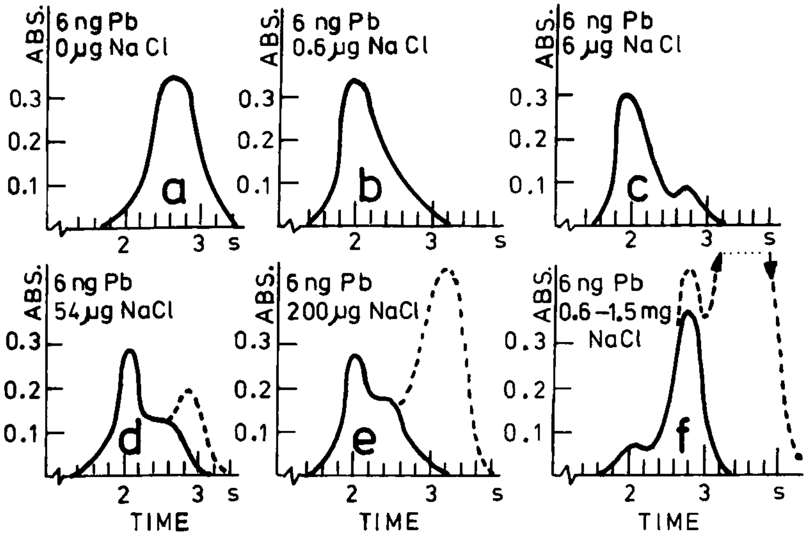

Fig.3. Effect of the NaCl concentration on the shape and time evolution of lead atomization peak.

by graphically averaging a series of recordings displayed on the 551 Video CRT when 4 ng of lead were atomized in a SCTA at 2600 °C (Ash 600°C; 30 s).

Some general remarks can be made on the atomization of lead at different concentrations of NaCl.

In the presence of low to moderately high relative concentrations (10^2 to 10^4 fold excess over analyte) of NaCl both peak time and rise time are shorter (Fig.3, b-e) with respect to the same parameters as obtained for the atomization of pure aqueous $Pb(NO_3)_2$ (Fig.3-a).

For moderately high (10^3 - 10^4) NaCl to Pb ratios there is a double peak and the reproducibility is deteriorated (Fig.3, c-e).

The Ash step has a marked influence on the atomization peak shape. If this step is cancelled or too low a temperature is selected, a double peak is recorded even at low concentrations of NaCl. The second peak can be attributed to the lead not converted into $PbCl_2$. The reproducibility of these peaks is poor because lead is only partially converted to $PbCl_2$ during the early stage of the atomization step.

When very high relative concentrations (10^5 fold) of NaCl to Pb are reached, the original peak corresponding to the atomization of pure $Pb(NO_3)_2$ is apparently restored (Fig. 3,f).

The efficiency of the background corrector was tested with 6 ng Pb in 1500 µg NaCl by selecting in the sample channel (A) the 280.2 nm Pb nonabsorbing line: only the background correction channel (B) displayed a peak during the atomization step.

The above mentioned general remarks hold true even with CLP and CTA, at different atomization temperatures, and using Ar or H_2 as purge gas.

It seems that the already complex mechanism of halide interference on lead has to be completed with this rather peculiar "restoration" of the original peak at very high concentration of NaCl. Although unnoticed by the authors themselves this effect seems to be also present in the records of an excellent paper by Czobik and Matousek[18], where some "restoration" of the original peak can be observed over 10 µg of NaCl. From the same study a shift of the NaCl vaporization time from 1.25 s to 1.9 s can be noted when the NaCl concentration is increased from 0.2 to 10 µg. It is hard to establish whether the lead peak time actually "restores" to the original

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value (1.8 s in that study[18], respectively 2.7 in this study) or, more probably, this value is dictated by the moment of NaCl vaporization (1.9 s that study[18], respectively 2.8 s this study). In more speculative terms it is probable that the bulk of NaCl plays the rôle of a secondary L'vov's Platform, further delaying the atomization, by an occlusion effect, to a moment when a higher temperature exists in the tube.

What is definitely sure is the fact that the Slevin's and Manning's[20] assertion: "lead vaporization takes place every time at a temperature which depends on the matrix" is to be completed: "*and of the concentration of the matrix*".

The use of H_2 as purge gas did not result in an alleviation of interferences[19] probably because this approach can remove only limited amounts of chlorides by volatilization as HCl but cannot be effective when the analyte is swamped in NaCl. The peak evolution is faster in H_2 than in Ar (e.g. the peak time for lead is 1.3 - 1.4 times shorter in H_2). This can be accounted for by the high heat capacity and thermal conductivity of the H_2 which improves the heat transfer processes; also due to the low viscosity and the high diffusion coefficient of H_2 the atom cloud rapidly diffuses out of the tube. No explanation could be found so far for the less noisy base line recorded when a clean tube is heated in a hydrogen atmosphere than in an argon atmosphere.

As far as the atomization of lead in a NaCl matrix is concerned the CLP, CTA and the SCTA compare well to other atomizers described in the literature. However, the aim of this paper is to evaluate their capability to atomize lead from solid air particulates. Since the concentration and the composi-

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tion of a natural aerosol is subjected to temporal variations it is difficult, at least theoretically, to obtain two identical samples by air sampling unless two identical samplers are operating at the same time. Therefore an indirect approach was used. Air particulates collected on cellulose nitrate filters were ultrasonated in Methyl-iso-buthyl-ketone (MIBK) and a liquid suspension was obtained[15]. Since the cellulose ester does not affect the atomization processes[15], the deposit left behind after the evaporation of MIBK and the ash of cellulose nitrate reasonably reproduces a deposit obtained by electrostatic precipitation. The advantage of this approach is that a large quantity of homogeneous suspension can be prepared, and many aliquots are available for analysis by different techniques.

The air particulate samples collected in an urban atmosphere contain a high level of lead of anthropogenic origin (up to 2-3%) and most of lead containing species (chlorides, bromides, chlorobromides, oxides, carbonates) present in such an atmosphere are easily atomizable species. Therefore more complex air particulate samples, collected over the Romanian branch of the Background Air Pollution Mondial Network (BAPMoN), were used as MIBK surpensions.

Table I summarizes the lead recoveries obtained with different furnaces from a selected particulate sample that displayed a low recovery figure with the standard SP 9-01 tube.

The chemical pretreatment of the sample by addition of HNO_3 (d=1.42) directly into the graphite furnace resulted in a broader atomization peak (Fig.4-a). Initially, HNO_3 was suspected to promote some secondary reactions between lead and

TABLE I

(% recovery of Pb in air particulate samples)

	Acid decomp.	MIBK suspension (d)
L'vov Platforms	59%(a)	75%
CTA	42%(b)	77%
SCTA	71%(a)	77%
Standard Tube	(c)	38%

(a) - Decomposition in Teflon Bomb with : $HF + HClO_4 + HNO_3 + H_2O$(1 + 1 + 5 + 20)

(b) Decomposition in open vessel with: $HClO_4 + HF$ (1+1), and finally with HNO_3 (d=1.42)

(c) Erratic signals when the final solution is high in acid

(d) Percent ratio of the value obtained using direct calibration with $Pb(NO_3)_2$ in H_2O-dioxane-MIBK solution, with reference to the value obtained by PTFE bomb decomposition and standard addition considered the best estimation. A recovery test would be meningless because the added lead stays outside the aerosol particle and does not react with the concommitants except for a monolayer at the particle surfce or in gas phase

matrix concommitants resulting in high thermal stability species. However, the same deterioration of the atomization peak (Fig. 4-b) was obtained by the action of HNO_3 (d=1.42) on a pure $Pb(NO_3)_2$ sample. If carbon reduction of lead oxide is the principal mechanism responsible for the generation of lead atoms[22], then it is probable that HNO_3 action results in a deactivation of the reducing properties of the graphite.

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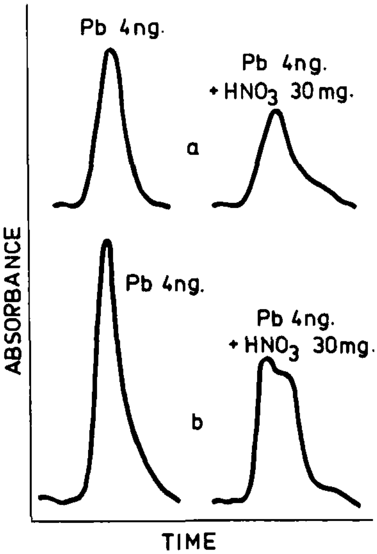

Fig.4. Influence of the nitric acid on the peak shape: a - natural sample of atmospheric particulates; b - synthetic sample of aqueous lead nitrate. (Carbidized CTA or L'vov Platforms)

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The better estimates obtained by direct calibration when the sample is introduced as MIBK suspension suggest an analogy with the FASTAC system[21]. Better recoveries were obtained when the sample was sprayed as an aerosol onto the hot wall of the furnace (FASTAC) than when using discrete samples (manual pipetting). It seemes reasonable to assume that the high area/volume ratios of both natural aerosols and nebulization produced aerosols would result in a better heat transfer to the sample.

Although better lead estimates were obtained for the solid aerosol with delayed furnaces, direct calibration is still not recommended. The standard addition is not only questionable (Table I, note d) but also difficult to operate with as the unique and the indivisible sample obtained by electrostatic precipitation, unless a sequence of time differing samples, is considered a series of aliquots. The solution to this problem seemes to be the direct calibration with a standard matching as much as possible the physical and chemical properties of the sample. A secondary solid standard obtained by pooling a large number of samples suspended in a suitable solvent would be a reasonable alternative[15].

The described delayed atomization furnaces for electrostatic precipitation of air particulates are a better alternative to standard furnaces and can be operated on commercial AA equipment, and with a little ingenuity and engineering the system can be adapted for automatic sequential analysis[23].

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