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Speciation of Organolead Compounds in Air by GC–MS–SIM

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A procedure for trapping tetraalkyl-lead (TAL) compounds in air is described. The system consists of a solid cartridge containing a mixture (65:35, w/w) in series of Porapak and Tenax. A contaminated atmosphere with a known concentration of TAL was generated in the laboratory. This atmosphere was trapped in the solid cartridge. After passing synthetic air through the system, the cartridge was extracted with hexane in an ultrasonic bath. The organic extract was concentrated under nitrogen current and the compounds were analyzed by GC–MS–SIM.

Each step of the process was studied independently. Losses of volatile compounds in the evaporation step, the storage of the cartridge over 45 days before the extraction step and the breakthrough volumes have been established in order to achieve optimization of the whole process. The analytical conditions of the final quantification include a linear range between 1.32 pg and 50.10 ng for Et_4Pb, and 5.30 pg and 51.40 ng for Me_4Pb. The detection limits are 0.66 pg, 3.40 pg, 1.07 pg, 1.05 pg and 2.60 pg for Et_4Pb, Et_3MePb, Et_2Me_2Pb, $EtMe_3Pb$ and Me_4Pb, respectively.

Keywords: Lead speciation, tetraalkyl-lead, alkyl-lead, organolead, air sampling, environmental air, solid adsorbents

INTRODUCTION

As a result of their use as gasoline additives, tetraalkyl-lead (R_4Pb) compounds continue to be emitted into the atmosphere,[1] where they decompose forming trialkyl-lead (R_3Pb^+), dialkyl-lead (R_2Pb^{2+}) and eventually, inorganic lead (Pb^{2+}) aerosol.[2] In addition, evidence for the natural formation of alkyl-lead compounds from inorganic lead in the environment is available from several sources and more recent studies have shown good evidence that the oceans act as a large-scale natural source of alkyl-lead in the atmosphere.[3]

In view of the dissimilar toxic properties of different tetraalkyl-lead (TAL) species,[4] data for their concentration in the atmosphere are necessary for a full assessment of the health hazard. For this reason, the demand for accurate, reliable and sensitive techniques for the monitoring of TAL in the atmosphere has increased recently. The reasons include not only a growing concern for the quality of the environment but also the realization that atmospheric pollution is not only a local problem.

Several procedures have been proposed for sampling TAL in the atmosphere. Most of them are focused on cryogenic trapping,[3,5,6] absorption in a solvent followed by concentration on a reversed-phase column,[7] adsorption on a porous polymer at ambient temperature[8–10,11] or the use of activated carbon[12] as a system to trap tetramethyl-lead and tetraethyl-lead compounds from the air. However, the collection of other alkyl-lead compounds in the air has received less attention.

On the other hand, the speciation of these TAL compounds has been carried out by separation of the species by capillary gas chromatography as well as high-performance liquid chromatography (HPLC) followed by detection and determination with an element-specific detector. Most of the published papers deal with the atomic absorption spectrometer (AAS) as detector[13] and recently the use of an atomic emission spectrometer (AES) coupled to GC has been described for the speciation of organolead compounds.[14]

Although other available systems that are easy to use, such as GC–MS, can be employed for speciation analysis of organolead compounds, they have received less attention.[15,16]

This paper presents a study carried out with the five TAL compounds. A contaminated atmosphere of a known concentration of each TAL was generated in the laboratory and trapped on a combined solid bed of Tenax and Porapak in

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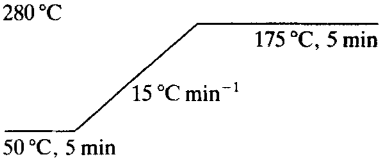
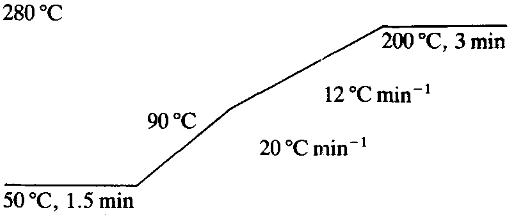
Table 1 Chromatographic conditions

Column	Capillary SPB-1 30 m × 0.25 mm i.d. × 0.25 μm				Capillary DB-5 60 m × 0.25 mm i.d. × 0.25 μm			
Injection volume	2 μl				2 μl			
Injector temp.	250 °C				250 °C			
Detector temp.	280 °C				280 °C			
Column program								
Solvent delay	3 min				5.7 min			
Carrier gas	Helium: 50 kPa head pressure				Helium: 110 kPa head pressure			
	Group	Retention time (min)	Start time[a] (min)	*m/z*	Group	Retention time (min)	Start time[a] (min)	*m/z*
SIM mode	Me_4Pb	4.15	1.0	208, 223, 251	Me_4Pb	6.68	1.0	208, 223, 251
	Me_3EtPb	6.83	6.0	208, 223, 253	Me_3EtPb	7.80	6.0	208, 223, 253
	Me_2Et_2Pb	8.95	8.3	208, 223, 267	Me_2Et_2Pb	9.20	8.3	208, 223, 267
	Me_3EtPb	10.59	10.1	208, 223, 281	Me_3EtPb	10.62	10.1	208, 223, 281
	Et_4Pb	11.94	11.5	208, 237, 295	Et_4Pb	11.94	11.5	208, 237, 295

[a] Time at which the detector was turned on and began to measure.

series. The compounds were extracted with hexane and the organic extract, after being concentrated, was analyzed by GC–MS–SIM.

EXPERIMENTAL

Reagents

The standard solutions were prepared in hexane (Merck, for residue analysis quality) with commercially pure Me_4Pb, Me_3EtPb, Me_2Et_2Pb and $MeEt_3Pb$ (supplied by Associated Octel Company Ltd), and Et_4Pb (supplied by Alpha Ventron). The solid adsorbents Porapak and Tenax were supplied by Supelco. Cylinder synthetic air N-50 (SEO—Sociedad Española de Oxígeno) was of 99.999% purity.

Apparatus

Sampling tubes

Glass tubes (110 mm × 6.4 mm i.d.) with a tapered end and packed with 35 mm of each adsorbent—(Tenax and Porapak (35:65, w/w) placed in series with silanized glass wool at each end—were used for collection of the analyte.

GC—MS

An HP 5890 series II with a DB-5 capillary column, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness, and a 5971A mass selective detector were used. The chromatographic conditions are included in Table 1.

Alternatively, an SPB-1 capillary column of 60 m × 0.25 mm i.d. × 0.25 μm film thickness was used.

Procedures

Generation of the standard atmosphere

A synthetic contaminated atmosphere containing a known concentration of TAL was generated in the laboratory using the oven of a GC and a hollow glass column of silanized glass (0.25 in i.d. × 2 m). Then a 100 μl portion of hexane solution containing 0.5 μg g^{-1} of each of Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$ and Et_4Pb was injected into the hollow glass column. Cylinder synthetic air at a flow rate of 1 l min^{-1} was used as carrier gas. The oven temperature was held at 60 °C to avoid fast evaporation of the volume injected. A small amount of silanized glass wool was placed inside the column to facilitate the homogeneity of the evaporation step.

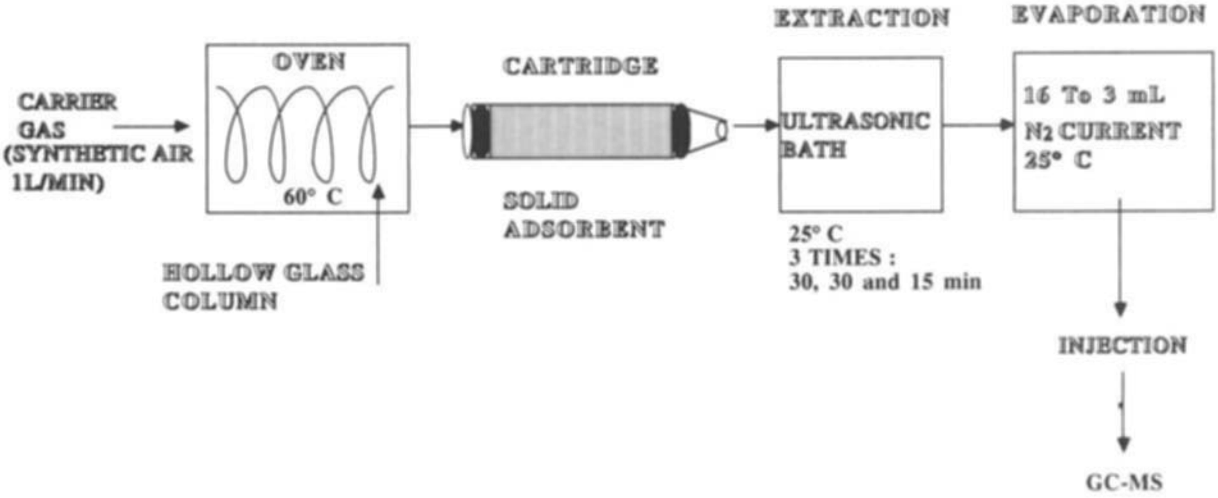


Figure 1 Scheme of the system used to study the adsorption capacity.

Trapping procedure for TAL

A glass cartridge containing the two adsorbents (Tenax and Porapak) in series was placed in the oven outlet; 40 min after injecting the solution into the empty column, the temperature of the oven was increased to 150 °C for 10 min, to ensure that all the sample was evaporated. Once the trapping step was finished the solid adsorbent was extracted three times with 4 ml of hexane in an ultrasonic bath. The 16 ml (including 4 ml of washings) of extract obtained was evaporated down to 3 ml under a current of nitrogen at 25 °C. Finally, 2 µl of this latter solution was analyzed by GC–MS–SIM. All the calculations were carried out on the basis of gravimetric calibration. The flow scheme is shown in Fig. 1.

RESULTS AND DISCUSSION

Speciation analysis of organolead compounds

The technique used for the speciation and quantification of alkyl-lead compounds makes use of a gas chromatograph (GC) connected to a mass spectrometer detector of the quadrupole type. The separation of the five alkyl-lead compounds was carried out on a nonpolar column (SPB-1). However, sufficient separation of all the peaks was obtained using a slightly polar column such as DB-5 as well. This fact suggests that the chromatographic separation of these compounds in capillary columns is not very critical. Figure 2 shows the chromatograms obtained with a standard solution of TAL in hexane.

In order to obtain the maximum sensitivity and specificity in the analysis of R_4Pb, three mass units were selected for each compound and the SIM mode was used in all the work. These mass values are shown in Table 1.

To establish the linear range for each compound, several solutions of increasing concentration were injected into the system. The ratio between the response obtained measured as peak area and the mass injected was plotted versus the mass injected. Figure 3(a) shows the results obtained. It can be observed that all of them are linear in the ranges studied. No differences were found in the responses of the detector at very low concentration levels. On the other hand, when the detector response obtained is plotted against the mass injected, a linear calibration graph is obtained, as can be seen in Fig. 3(b). The comparison of the slope of the calibration graphs of all the compounds can give an indication of the different sensitivity of the detector to each compound. According to this, Et_4Pb is the most sensitive.

Following IUPAC recommendations, the detection limit was considered as the concentration equivalent to three times the background signal, at the selected masses of each compound. This background signal (s) was obtained when a blank solution was injected into the GC–MS under the same conditions as the sample. Taking

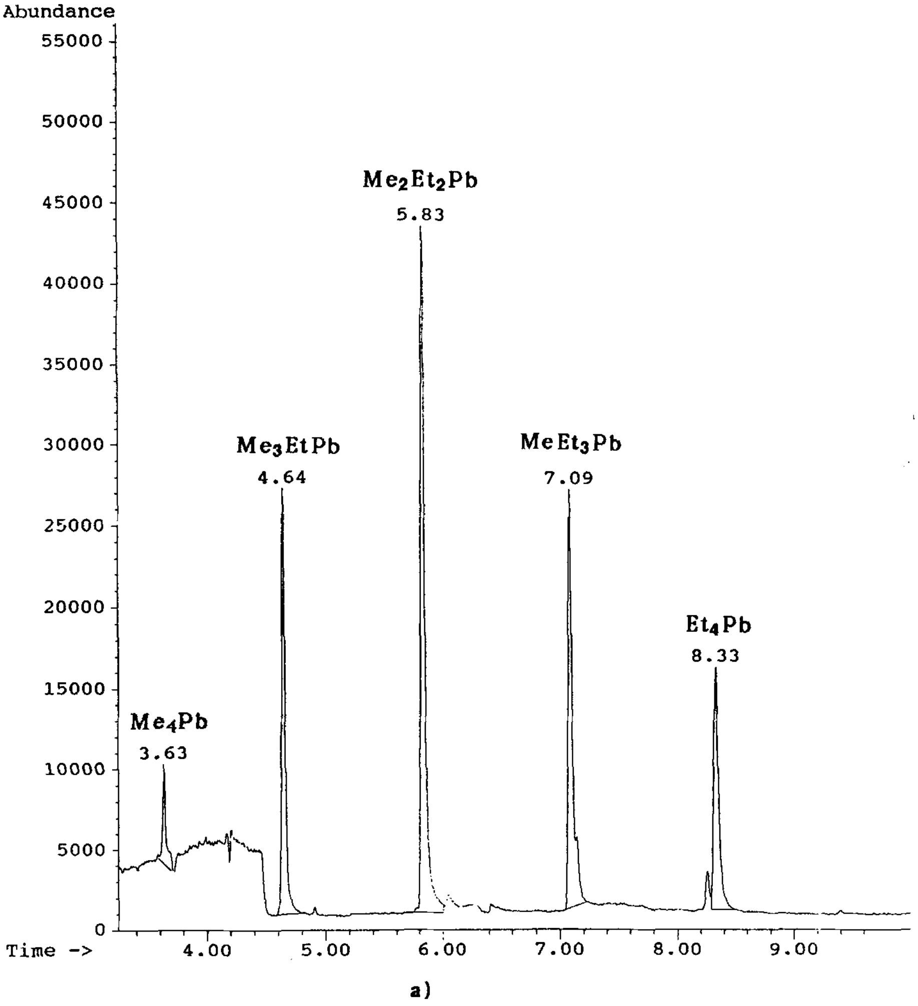


Figure 2a GC–MS–SIM mode chromatograms of a hexane solution of diluted gasoline (1:100) from Zaragoza containing 0.4, 1.0, 1.7, 1.2 and 4.5 μg g^{-1} of Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$ and Et_4Pb, respectively.

into account the standard deviation of this background signal, the value was obtained as follows:

$$s = \bar{x} + 3\sigma_b$$

where $\bar{x}$ is the average value of the background noise and σ_b is the standard deviation of the blank, obtained when a blank solution was injected into the GC–MS five times under the same conditions as above.

In the first instance these values were obtained with standard solutions. However, after the whole procedure had been optimized, the limits were calculated again and no differences were observed. This agrees with the selectivity of the selected ion monitoring (SIM) mode, in which only the selected masses are analyzed. Clearly, when no compound interferes at the same retention time in the chromatogram, the baseline is not modified and, consequently, the background noise can be considered constant.

As can be seen in Table 2, the detection limits are expressed on the basis of the total amount injected into the GC–MS. The quantification limit has been considered as the minimum value which can be quantified with a minimum error. This value was the minimum concentration level in the calibration graph. Clearly this value is higher than the detection limit, as can be seen in Table 2.

It is noteworthy that, in contrast to other procedures published for lead speciation analysis, the

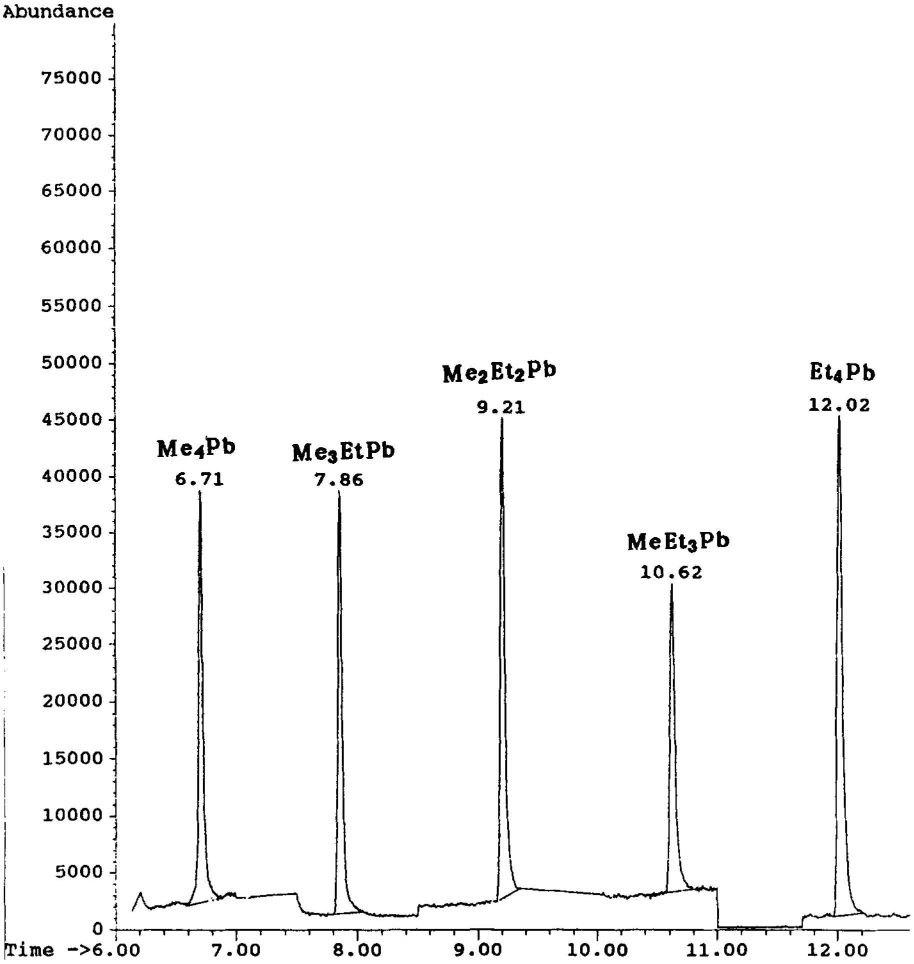


Figure 2b GC–MS–SIM mode chromatograms of a hexane solution of a mixture of the five standard TAL (30 ng g^{-1}).

use of the GC–MS–SIM mode makes it possible to determine all the tetraalkyl-lead compounds within the same GC run and with a very good sensitivity.

The use of the SIM mode avoids interferences and enhances the advantage of this analytical method.

Compared with other existing methods used for speciation analysis, such as the hyphenated techniques GC–AA or HPLC–AA, the analysis of alkyl-leads by GC–MS is more sensitive, easier and cheaper.

The organic extract can be placed in an autosampler connected to the GC–MS and the instrument runs may be left unattended. Unattended analysis is much more difficult with the other systems mentioned.

Extraction and evaporation steps

Once the compounds were adsorbed on the solid cartridge, they were extracted with hexane in an ultrasonic bath. Due to the relatively high volatility of the TAL compounds, Soxhlet extraction is less efficient than ultrasonication at 25°C. Another advantage of ultrasonic extraction is the lower volume of solvent necessary compared with that employed in the Soxhlet method. However, in both cases an evaporation step is essential to obtain a more concentrated extract. As a result of the volatility of the compounds, this evaporation step can be critical in the recovery of the compounds, as was shown in previous work.[15] To study the influence of this step in the total recovery of the compounds, several standard solutions in hexane were evaporated under a nitrogen current at 25 °C to different final small volumes and the compounds were quantified. by GC–MS–SIM. Figure 4 shows the results obtained. It can be observed that evaporation losses increase when the final volume decreases and this relationship is nonlinear. Tetramethyl-lead, the most volatile, is the compound most affected, which means that, if the final volume to which the extract is evaporated is less than 3 ml, the loss of TML would be higher than 30%. This behavior has been previously described with other compounds.[17] Consequently, the final volume of the organic solution containing the compounds should be limited to a maximum value of 3 ml. Obviously, to achieve quantitative results, the final values obtained should be corrected for this behavior.

Storage of the solid cartridge

The instability of alkyl-lead compounds has been described in previous papers. This instability mainly produces the ionic alkyl-lead compounds but it is important to know what happens when their precursor TAL compounds are adsorbed on a solid bed which is stored before extracting. In effect, when the atmosphere is monitored, the solid cartridges are not immediately extracted, which means that these solid beds with the orga-

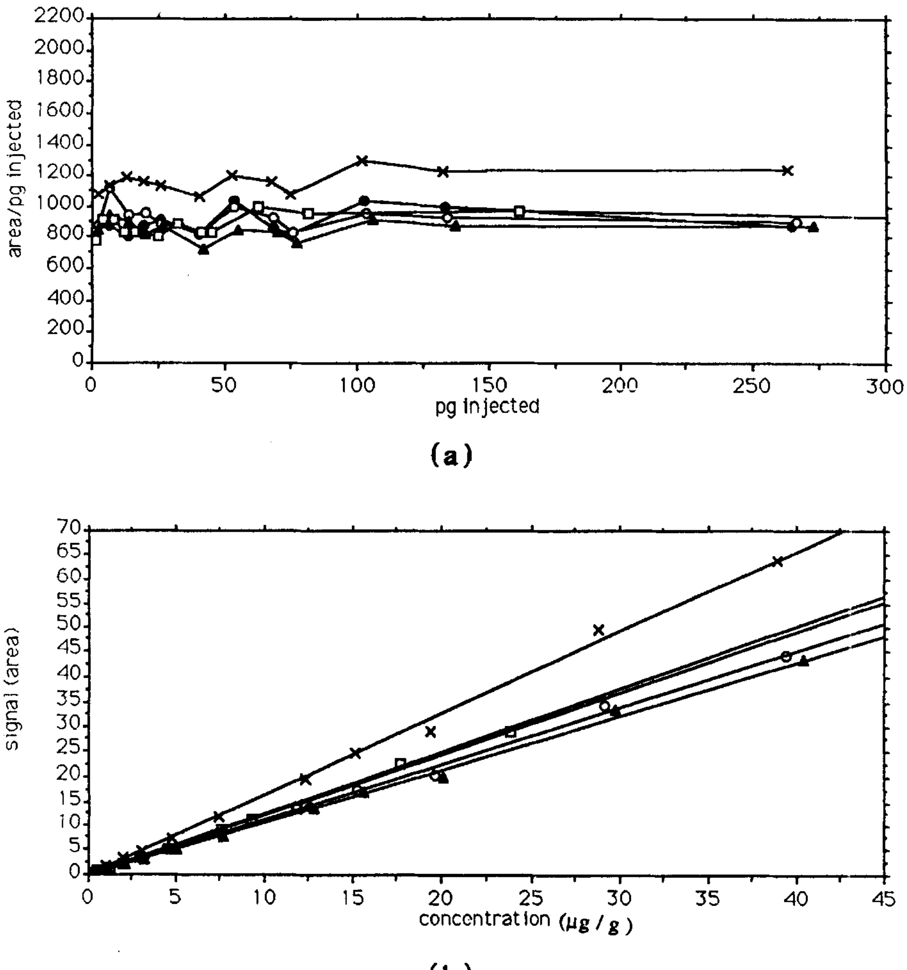


Figure 3 Linear range and sensitivity of the detector: (a) signal/mass injected versus mass injected; (b) signal versus concentration: ●, Me_4Pb; ○, Me_3EtPb; ▲, Me_2Et_2Pb; □, $MeEt_3Pb$; ×, Et_4Pb.

Table 2 Sensitivity and linear range

Compound	Detection limit (pg)[a]	Quantification limit (pg)[a]	Linear range
Me_4Pb	2.60	5.30	5.30 pg–51.40 ng
Me_3EtPb	1.05	2.64	2.64 pg–51.40 ng
Me_2Et_2Pb	1.07	2.64	2.64 pg–52.80 ng
$MeEt_3Pb$	3.40	2.64	2.64 pg–31.40 ng
Et_4Pb	0.66	1.32	1.32 pg–50.10 ng

[a] Total mass injected into the chromatograph.

nolead compounds are kept in a refrigerator at 4 °C, perhaps for several days, before use.

In order to study possible losses of TAL due to the storage of the solid bed, several cartridges were prepared by generating the contaminated TAL atmosphere. Two of them were immediately analyzed and the others were stored during different periods of time (from 1 to 45 days), after which they were extracted and analyzed under the procedure mentioned in the Experimental section. Table 3 shows the results obtained. It can be observed that no significant differences were obtained. In these conditions none of the compounds studied seems to be unstable.

Breakthrough

To obtain the breakthrough volume for each compound, the recommended procedure was followed, but with a second cartridge connected in series with the main cartridge. Both solid beds were independently extracted and analyzed. The synthetic air flow was increased in each experiment so that, once the breakthrough volume was exceeded, the compound could appear in the second cartridge. The breakthrough volumes depend very much on the surface area of the solid in which the compounds are trapped. As Tenax and Porapak together were used as the trapping system, they have different surface areas and consequently the breakthrough volumes can vary with respect to those obtained with both adsorbents separately. Tenax has a low specific area, and a small breakthrough volume for volatiles can be expected compared with other adsorbents such as XAD resins or Chromosorb resins.[18,19] With the exception of tetramethyl-lead, breakthrough volumes were not achieved even though a volume of 360 l of synthetic air passed through the cartridge when a total amount of 33 ng of each organolead compound was trapped. Tetramethyllead (4 ng) was found in the second cartridge when 70 l of synthetic air passed through the cartridge. These results agree with those mentioned in the literature.

Determination of alkyl-leads in the atmosphere

Once the method for sampling and analyzing organoleads in the air was optimized in the laboratory, a study on a real atmosphere was carried out. The combined cartridge containing Tenax and Porapak was connected in series in the inlet of a low-volume monitor in which a pump was running at 1.5 l min^{-1}. This monitor was placed in an urban area of high population density in Zaragoza city, Spain, where the traffic is quite heavy. The monitor was pumping the air through the cartridges for 24 h, and in these conditions 2.16 m^3 of air was passed through the solid bed.

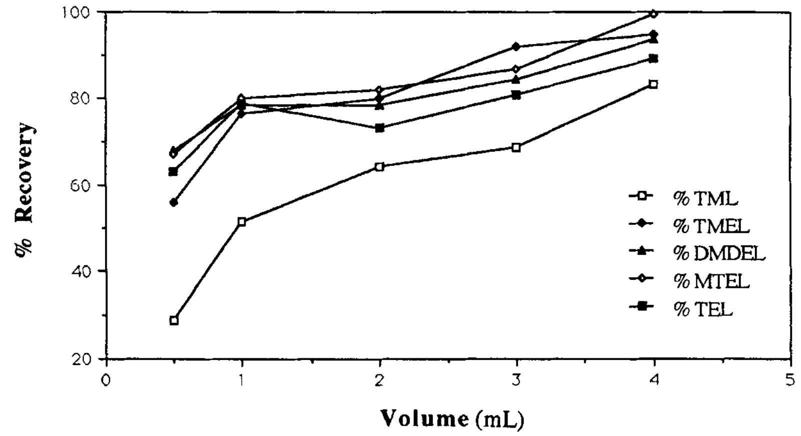


Figure 4 Recovery of TAL (%) versus final volume in studies on the concentration by evaporation of hexane solutions under a current of nitrogen. □, Me_4Pb; ◆, Me_3EtPb; ▲, Me_2Et_2Pb; ◇, $MeEt_3Pb$; ■, Et_4Pb.

Table 3 Recoveries obtained (%) with different cartridge storage times

t (days)	Me_4Pb	Me_3EtPb	Me_2Et_2Pb	$MeEt_3Pb$	Et_4Pb
0	96.4	93.4	96.2	95.4	94.0
15	93.4	75.6	95.1	74.9	91.3
30	85.2	92.2	99.0	72.7	79.1
45	84.9	113.5	85.6	88.4	95.0

Following the optimum procedure mentioned above the final extract was analyzed by GC–MS. In scan mode, numerous compounds, mainly benzene derivatives such as 1,2,3-trimethylbenzene, 1,2-diethylbenzene and related compounds, were found. These compounds could be attributed to car and lorry exhausts. When the same extract was analyzed in SIM mode, with the selected masses corresponding to the alkyl-leads, only one of them, Me_2Et_2Pb, was found. This result agrees with the real situation, as this compound is the most abundant in the lead gasoline used in the area and, consequently, it should be the most abundant alkyl-lead in the atmosphere when working under the conditions specified above. A value of 3.4 ng m^{-3} was obtained for Me_2Et_2Pb

These results confirm the validity of the proposed method for sampling organoleads in the atmosphere, with a high sensitivity.

CONCLUSIONS

The study has demonstrated the possibiliyt of a rapid and very sensitive speciation analysis of organolead compounds in air. The combined bed of Tenax and Porapak in series offers clear advantages of easier air sampling and lower losses compared with other existing procedures. Although the cartridge used for trapping TAL is quite small (70 mm of solid bed), its efficiency is very high. On the other hand, the use of GC–MS in SIM mode has been shown as an excellent analytical technique for speciation analysis and the sensitivity is better than that described by other methods. The linear range is accomplished from a few picograms to several nanograms for all the compounds.

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