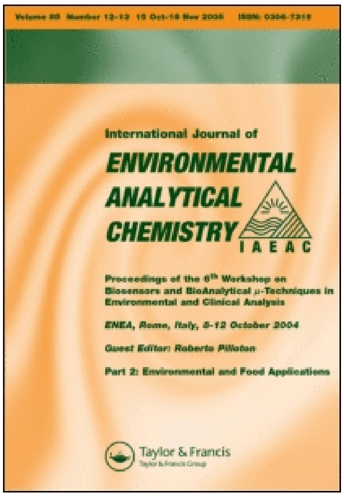

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CHARACTERIZATION OF AEROSOL-ASSOCIATED LEAD BY DPASV AND LAMMA

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Both a bulk-analytical and a micro-analytical technique were used to determine lead in standard particles and natural aerosols. The localization of lead within standard particles was successfully studied. Both techniques were able to discriminate between particles which were coated with lead and particles with a homogeneous lead(II) distribution.

Total lead present in aerosols was successfully quantitatively determined with Differential Pulse Anodic Stripping Voltammetry (DPASV), X-Ray Fluorescence (XRF) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The results from the different techniques are in good agreement. DPASV was also used to obtain information about the lability of lead associated with the aerosol particles. The observed potential shifts indicate that lead forms labile complexes with the chemical groups of aerosol particles. With Laser Microprobe Mass Analysis (LAMMA), information on single particle composition was obtained. Most particles were mixed salts of ammonium nitrate and ammonium sulphate, with variable content of metals (especially V and Pb).

KEY WORDS Lead, aerosol, lability, bio-availability, DPASV, LAMMA.

INTRODUCTION

Lead may be present in atmospheric aerosols, either homogeneously distributed within the particles or enriched at the surface after condensation from the gas phase. The health risk of lead in aerosols depends on the ease by which lead is liberated from the particle, i.e. on the bio-availability. For non-dissolving particles it seems reasonable to assume that lead coming from lead-coated particles is more easily liberated than lead originating from particles with a homogeneous lead distribution.

There may also be a relation between the bio-availability and the so-called lability of the lead-aerosol 'complex'. The definition of lability used here is an electrochemical one: the rates of dissociation and association of the aerosol complex are so high that the observed response is purely controlled by the coupled diffusion of free and complexed lead. Lability is characterized by a shift in reduction potential of lead towards more negative potentials and effected by the difference in diffusion coefficients of free and particle-bound lead.[8,9]

In this context, the aims of the present investigation are:

- Direct determination of the total amount of lead(II) present in aerosols using Differential Pulse Anodic Stripping Voltammetry (DPASV) in comparison with other techniques such as Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and X-Ray Fluorescence (XRF)[2].
- Distinction between model aerosol particles with lead only at their surfaces, and particles with homogeneous lead distribution, using the bulk-analytical DPASV method and the single-particle laser microprobe mass analysis (LAMMA). Localization of lead associated with real atmospheric aerosol samples.
- Determination of the lability characteristics of the lead-aerosol associate using DPASV.

MATERIALS AND METHODS

Preparation of standard particles

All chemicals used were of analytical grade (Merck).

Preparation of coprecipitated lead/calcium carbonate particles (homogeneous lead distribution). 200 ml of a 0.05 M $Ca(NO_3)_2$ and 50 μM $Pb(NO_3)_2$ solution were added dropwise to 100 ml of a 0.1 M Na_2CO_3 solution at 37°C. Stirring was continued for 24 h, in order to obtain a suspension with a particle size of about 30 μm. The resulting suspension was filtered under vacuum on a cellulose acetate filter (pore size 0.3μm) and washed 3 times with demineralized water (Millipore Super-Q reverse osmosis system). The salt was freezedried for 15 h[6].

Preparation of coated lead/calcium carbonate particles (heterogeneous lead distribution). $Ca(CO_3)_2$ powder was sieved using metal sieves with hole sizes of 32 and 53 μm; 2 g of particles with a size between 32 and 53 μm were added to a solution of 100 ml 10 μM $Pb(NO_3)_2$. The suspension was stirred for 25 min and then filtered and dried as described in the preparation of coprecipitated lead/calcium carbonate particles[6].

Sampling of natural aerosols

Aerosols, collected on Whatman 4.2 cellulose filters in Vlaardingen, The Netherlands, were kindly provided by RIVM in Bilthoven[2].

The samples collected on filters could not be used for LAMMA; therefore additional aerosol material was sampled. Aerosols were collected at two locations: at the Transitorium, Dreijenplein, Wageningen, The Netherlands, and at the downwind site of the A12 highway at Ede, The Netherlands. These samples were obtained by means of a three-stage Berner Cascade impactor equipped with Formvar (i.e. a slightly adhesive polymer)-coated electron microscopy grids, operated at a flow rate of maximum 0.3 l/min. The corresponding 50% cut-off aerodynamic diameters of stages 1–3 are 0.1 µm, 0.9 µm and 2.9 µm respectively. A sampling time of 1 min provided a satisfactory aerosol loading for LAMMA measurements. At the same time, aerosol material was collected on Whatman filters, for bulk-analytical lead concentration measurements with DPASV to obtain an idea of the lead concentration in the sampled air.

Experimental

DPASV measurements. DPASV was performed using a hanging mercury drop electrode (Metrohm 663 VA Stand) and an Ag/AgCl reference electrode (potential 222.3 mV). All potentials are referred to this reference electrode. The stand was coupled to a polarograph (Autolab, Eco Chemie) and controlled by a computer (Hyundai Target AT 80286) using the programmes General Purpose Electrochemical System 3.0, and Electro Analytical System 2.0 for the standard addition method. Before measurements were performed, dispersions were purged for 600 s with water-saturated N_2 (technical grade), which had been led over a solution of 0.1 M KOH. A 25-ml measuring cell made of polystyrene was used. In case of smaller volumes and a pH of 2, a cell made of glass was used. The deposition time was 120 s and the deposition potential was –0.600 V.

Determination of total lead concentration. The following procedure was performed: 10 ml of a solution of 0.1 M KNO_3 pH 2 (adjusted with HNO_3) was added to one filter loaded with aerosols. KNO_3 was added, since DPASV requires an indifferent electrolyte to maintain a signal linear with the concentration of free lead. A high concentration of KNO_3 eases the liberation of lead(II). In this way, all the lead is liberated from the particle by destroying the aerosol particles. The resulting mixture was ultrasonificated for 1 h (Bandelin Sonorex super digital, 100%). Filter material was removed by centrifugation at 10,000 rpm for 10 min (Beckman JA20). The supernatant was measured with AAS and DPASV, performed with two or three standard additions of lead nitrate.

Determination of total lead concentration and lead fraction in model particles. It may be expected that in a dispersion containing lead-coated particles relatively more lead will be found in solution compared to a dispersion containing lead-coprecipitated particles. This effect can be used to discriminate between the two types of standard particles. In order to quantify the difference between the two types of standard particles, we use R:

$$R = \frac{\mathrm{HPb} / \mathrm{HPbt}}{\mathrm{CPb} / \mathrm{CPbt}} = \frac{\mathrm{HPb}}{\mathrm{CPb}} \times \text{constant} \qquad [1]$$

which is the ratio between the normalized voltammetric signals of coprecipitated lead and coated particles. HPb and CPb are the voltammetric signals for lead liberated from coprecipitated (i.e. *h*omogeneous lead distribution) and *c*oated particle dispersions, respectively. The t stands for the concentration of *t*otal lead. To improve discrimination, some methods to enhance R were studied. This enhancement can be reached in one way by dissolution of the particles shell by shell. Dissolving a thicker part of the lead-coated shell initially leads to a greater difference in absolute lead concentration in solution between the coated and the coprecipitated particles. The dissolution of parts of the surface of the particles can be achieved by adding nitric acid. Of course, the change of the voltammetric signal of lead(II) due to a decrease of pH has to be taken into account.

Another way of improving discrimination between the two types of particles is possible by liberating lead(II) from the surface of the particles without dissolving the surface step by step. The differences in free lead concentration between the two types of particle dispersion may be expected to be stronger because relatively more lead will be liberated from lead-coated particles than from lead-precipitated particles. Since the model systems used consist of calcium carbonate and lead carbonate, it is possible to liberate lead(II) without dissolving the shell, by applying a method based on their solubility products. The solubility products of $CaCO_3$ and $PbCO_3$ are $1.96*10^{-8}$ and $1.70*10^{-11}$ mol^2/l^2, respectively [10]. Hence, for a saturated equimolar $CaCO_3$ solution the concentration of lead will never exceed $1.2*10^{-7}$ M. After addition of Ca(II) in a saturated equimolar $CaCO_3$ dispersion, a precipitation of calcium carbonate will be formed, and the carbonate concentration will decrease. A decrease in carbonate concentration is expected to liberate lead(II) as a consequence of the solubility product of $PbCO_3$. Another effect of adding Ca(II) might be expected: a decrease of the pH of the dispersion, due to a decrease of the carbonate concentration. The voltammetric signal of lead is dependent on the pH and that has to be taken into account. A second consequence of the solubility constants of lead and calcium carbonate is that the experimentally observed Pb(II) concentrations will be confined to a certain range. This range is limited on one side by the solubility of the $PbCO_3$ and by the detection limit of the voltammetric method on the other. The detection limit of DPASV is $1*10^{-10}$ M. The pH is determined by the carbonate ions in solution: the pH at which the dispersion appeared to be in equilibrium is quite high, about pH 9. The voltammetric signal of lead(II) is dependent on the pH of a solution. Due to formation of lead hydroxyl complexes it is difficult to measure lead directly in a dispersion at such a high pH. This problem could be avoided by filtering the particle suspension and acidifying the remaining solution using nitric acid before measuring.

Hence the experiments were performed as follows:

To determine the total concentration of lead associated with the particles and the value of the constant in Eq. 1, 50 mg of both were separately dissolved into a solution of 25 ml 0.08 M KNO_3, pH 2 and measured directly.

In order to determine the difference between both types of particles, 50 mg of particles with a homogeneous lead distribution and 50 mg lead-coated particles were separately dispersed into a solution of 25 ml 0.08 M KNO_3, pH 9 (adjusted with KOH) and shaken for 1 h. The suspensions were filtered and HNO_3 was added to the remaining solution until a pH of 2 was reached.

In order to increase the discrimination between the two types of particles, nitric acid was used to dissolve a larger part of the carbonate particles. 50 mg of particles were dispersed in a solution of 25 ml 0.08 M KNO_3 and 0.4 mM HNO_3 which is about 10% of the acid necessary to dissolve the particles completely. This corresponds to a shell of ± 1 nm thickness. The final pH of this system was 7.1. The suspensions were filtered, the remaining solution was adjusted to pH 2 with HNO_3 and analysed.

Enhancement of discrimination was achieved in another way by ion displacement: 50 mg of particles with a homogeneous lead distribution and 50 mg lead-coated particles were separately dispersed into 25 ml solution of 0.08 M KNO_3, pH 9 (adjusted with KOH). $Ca(NO_3)_2$ was added to the dispersions to a final concentration of 100 μM and shaken for 1 h. The suspensions were filtered and the remaining solution was adjusted to pH 2 with HNO_3 and analysed.

Lability of lead in aerosols. Two series of experiments were performed: some filters containing aerosol were extracted using 0.1 M KNO_3 of pH 2 (with HNO_3) and some filters containing aerosol were extracted with 0.1 M KNO_3 without acid. In all cases, 10 ml of the extracting solution were added per filter and ultrasonificated for 1 h (Bandelin Sonorex super digital, 100%). Filter material was centrifuged at 10,000 rpm for 10 min (Beckman JA20). The supernatant was analysed by DPASV. Blank filters were extracted in the same way as aerosol-containing filters. Lead ions were added to their supernatant in roughly the same final initial concentrations as in the aerosol samples and this dispersion was used as blank. Also, a measurement of only lead nitrate in 0.1 M KNO_3 pH 2 (with HNO_3) was performed. The pH of the dispersion of aerosols without added nitric acid was about 5. The dispersions were measured using DPASV in the pH ranges from 2 to 9 and from 5 to 9, respectively. The pH was increased by intervals of 0.2 pH units by adding 0.01 M KOH.

LAMMA measurements. LAMMA was performed using a LAMMA-500^R instrument (Leybold-Heraus, Köln, Germany). Under microscopic control, individual particles can be selected and evaporated by a 15 ns pulse of a focused Nd-YAG laser. The laser power density can be reduced to 2% of its initial value by means of a 25-step attenuating filter system. The laser generated ions were accelerated into a time-of-flight mass spectrometer that can be operated in either the positive or negative ion detection mode. The ions were detected by an open Cu-Be secondary electron multiplier. The signal was fed into a transient recorder, processed and sent through to a personal computer for storage, mass calibration and integration. A more detailed discussion on LAMMA and its applications can be found in the literature[7,14].

A total of four samples was investigated, namely impactor stages 1 and 2 from both locations. To obtain information about the chemical composition of the atmospheric aerosol, 25–70 particles were randomly analysed on each grid. Mostly positive ion mode spectra were collected because they are advantageous for the identification of trace metals (e.g. lead). Negative ion-mode spectra provided additional information concerning certain anions.

By lowering the laser power density to a fraction of that needed for total evaporation and aiming the laser beam at the particle surface facing the mass spectrometer, we tried to obtain

Table 1 Comparison of different methods of total lead (μg/filter) determination.

XRF[a]	*GFAAS*[b]	*DPASV*[c]
3.9	5.1	4.1
3.4	3.7	3.7
2.4	3.2	2.4
3.5	2.7	2.8
9.1	8.0	8.1
2.0	2.1	2.0

[a] Measured on intact filter
[b] Measured in dispersion (pH 2)
[c] Measured in dispersion (pH 2)

particle surface information in order to be able to discriminate between particles with a homogeneous (coprecipitated) and heterogeneous (coated) lead distribution.

RESULTS AND DISCUSSION

Determination of total lead in aerosols

The agreement between the data from different techniques is highly satisfactory (Table 1). This means that the simple dispersion procedure (almost) totally removes lead from the aerosol particles and the filters. Hence DPASV of the acidified dispersion directly measures the total lead content. The lead concentrations measured in the sampled air masses at Wageningen (13/2/1992) and Vlaardingen (22/2/1989) are 0.07 (±0.02) μg/m^3 and 0.67 (±0.04) μg/m^3, respectively.

Determination of (total) lead and lead fraction in standard particles

The concentration of free lead in the dispersion of homogeneous particles is expected to increase less than the lead concentration in the dispersion with lead-coated particles after addition of calcium or hydrogen ions. This is exactly what Table 2 shows: DPASV can discriminate between lead-coated calcium carbonate particles and lead-precipitated calcium carbonate particles. Attempts to increase the discrimination by using nitric acid and Ca(II) led to an enhancement of R by a factor of 4.5 and 11.3, respectively, and could be called successful. The enhancing effect might even be enforced after adding more Ca(II), since the final concentration of Ca(II) in the dispersions was quite low. We further note that the concentration of lead in solution after addition of Ca(II) to the dispersion with lead-coprecipitated particles is lower than before the addition. A value in the order of 10^{-8} M is expected here. An explanation could be that after addition of Ca(II) lead(II) is built into the precipitating salt.

The salt used for making standard particles was $CaCO_3$, which means that this method is based upon the solubility constant of $CaCO_3$. Since the matrix in aerosols is undefined,

Table 2 Discrimination between lead-coprecipitated and lead-coated calcium carbonate particles using DPASV.

	Lead [M]		*R*
	coprecipitated	coated	
No addition	$1*10^{-8}$ ($\pm 0.2*10^{-8}$)	$3*10^{-8}$ ($\pm 0.5*10^{-8}$)	4
Ca^{2+} added	$2*10^{-9}$ ($\pm 0.5*10^{-9}$)	$4*10^{-8}$ ($\pm 0.5*10^{-8}$)	45
H^+ added	$1*10^{-8}$ ($\pm 0.2*10^{-8}$)	$1*10^{-7}$ ($\pm 0.1*10^{-7}$)	18

consisting of various salts and organic matter, it is unknown how much material will dissolve and whether a saturated concentration of a lead-containing salt will be reached. Although the aerosol system is much more complicated than the standard calcium carbonate particles system, adding Ca(II) might liberate lead(II) associated with aerosols without dissolving them by exchange of lead(II) associated with aerosols by Ca(II).

Lability of lead associated with aerosol particles

Measurements starting from pH 2. As Figure 1 shows, the currents for the three types of experiments are identical below pH 5. The curves decrease with increasing pH above pH 5. From pH 6 the hydroxide concentration reaches levels which give rise to the formation of

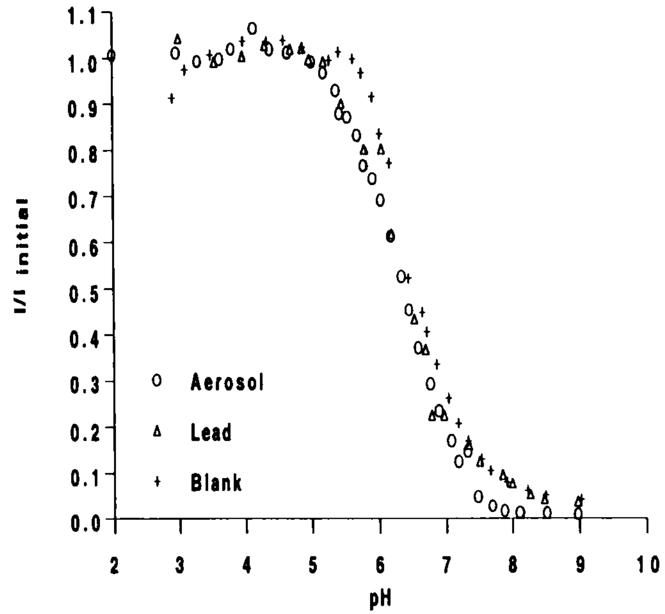

Figure 1 Normalized current of lead measured for a filter with aerosol, for a filter containing lead ('blank') and for a lead solution ('lead'), respectively, in a solution of 0.08 M KNO_3, initial pH 2, as function of pH.

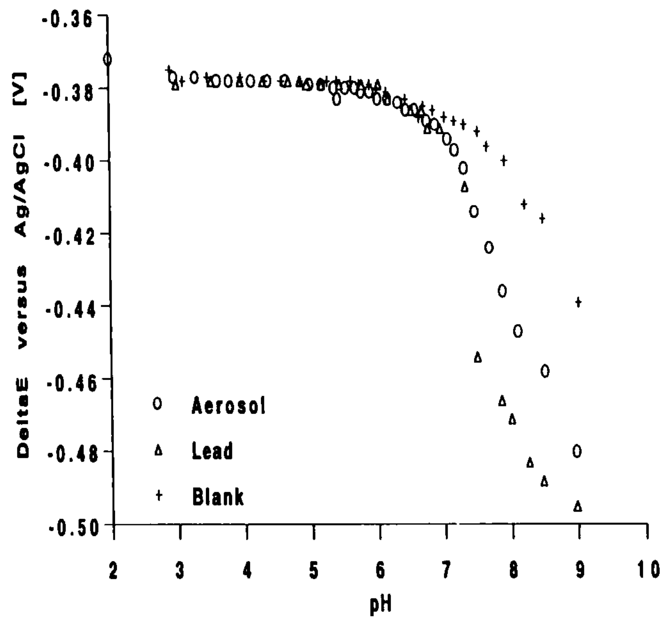

Figure 2 Reduction potential of lead measured for a filter with aerosol, for a filter containing lead ('blank') and for a lead solution ('lead'), respectively, in a solution of 0.08 M KNO_3, initial pH 2, as function of pH.

different lead-hydroxyl complexes, which are not fully labile. This is the cause of a lower signal at higher pH. There is no difference between the curves for blank filter with lead added, aerosol and only lead in solution. This seems to suggest that there hardly are interactions between lead ions and components such as chloride and sulphate originating from aerosols and/or filter. This explanation, however, does not agree with the reduction potential curves of Figure 2.

The reduction potential becomes significantly more negative above pH 6 for all curves in Figure 2. This is most evident for the solution with only lead ions. Again, this can be explained by the fact that at higher pH lead ions form hydroxyl complexes. The potential shift for solutions containing aerosols and/or filter material is less than in solutions without this material. Not all filter material can be removed by centrifugation. Therefore, we expected a higher potential shift than in solutions without this material due to adsorption of lead ions onto the (charged) groups of the filter and aerosol material.

Measurements starting from pH 5. Figure 3 shows that the curve for aerosols decreases more progressively as a function of pH compared to the other two curves. This is also true when the aerosol curve (Figure 3) is compared with the curves of Figure 1. The difference is most evident at pH 6. This is probably caused by the fact that at a pH above 6 lead-hydroxyl complexes start to form. At pH below 6, many chemical groups become uncharged by protonation and are less available as ligands for lead ions. The decrease in the aerosol curve above pH 5 in Figure 3 compared to Figure 1 might be caused by differences in diffusion

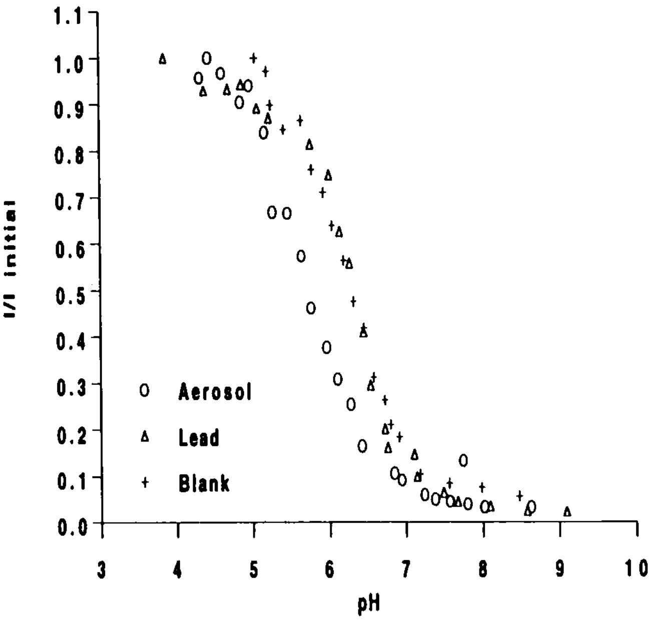

Figure 3 Normalized current of lead measured for a filter with aerosol, for a filter containing lead ('blank') and for a lead solution ('lead'), respectively, in a solution of 0.08 M KNO_3, initial pH 5, as function of pH.

coefficients, assuming a labile system. At pH 2 aerosols probably dissolve almost completely, since they consist of organic material and salts. When lead ions associate with ligands originating from aerosols, they associate with ions; the resulting complexes do not differ very much in diffusion coefficient from the free lead ion, associated with water and or nitrate. In the suspension prepared at pH 5, aerosols only partially dissolve and ligands are mostly attached to the aerosols, resulting in a smaller diffusion coefficient of a lead-ligand complex. A smaller diffusion coefficient results in a lower current, even in a labile system. These (in)organic complexes are labile: all curves in Figure 4 show a shift in potential at increasing pH. Again, we expected a higher potential shift for the solution containing filter materials, due to adsorption of lead ions onto the (charged), groups (originating) from the filter and/or aerosol material.

At pH 2, the total concentration of lead is measured. This means that a laborious preparation[13] to measure the total lead(II) concentration of aerosols is not necessary and that the simple method described here using DPASV is satisfactory. At pH 5, aerosols only partially dissolve, which means that only lead from the outer shell of the particle or from only certain types of particles is measured. Although it is not possible to calculate lead(II)/aerosol particle association constants until now, it should be possible to analyse aerosol particles shell by shell using DPASV just by titrating them with nitric acid in the range of pH 5 to pH 2.

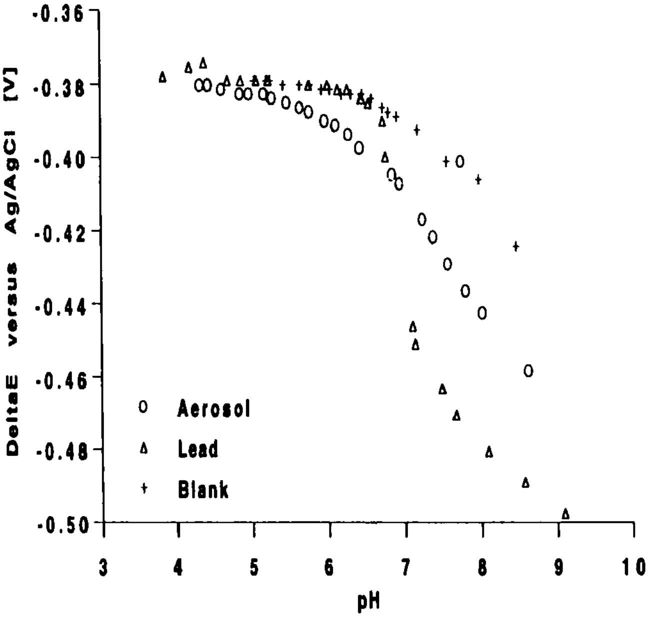

Figure 4 Reduction potential of lead measured for a filter with aerosol, for a filter containing lead ('blank') and for a lead solution ('lead'), respectively, in a solution of 0.08 M KNO_3, initial pH 5, as function of pH.

Determination of lead in standard aerosols (LAMMA)

Four different types of standard aerosols (Table 3) were prepared and analysed with LAMMA. Analysis of coprecipitated lead/calcium carbonate particles only resulted in calcium[5] and calcium oxide peak clusters. Even in the particles with the highest lead concentration, lead could not be detected. Calcium carbonate particles coated with lead did result in lead peaks.

Due to the large particle size, focusing the beam on the outer layers proved to be tedious. This rendered laser desorption practically impossible and particles were mostly blown away after a single laser pulse. Pb-coprecipitated particles were crushed in a mortar to a size of a few micrometers. This did not give satisfactory results either.

Table 3 Discrimination between lead-coprecipitated and lead-coated calcium carbonate particles using LAMMA.

Sample	*Procedure*	*Pb concentration (μg/g)*	*Particle size (μm)*
1	coprecipitated	920 ±40	<53
2	coated	660 ±40	<53
3	coprecipitated	440 ±40	<32
4	coated	280 ±40	<32

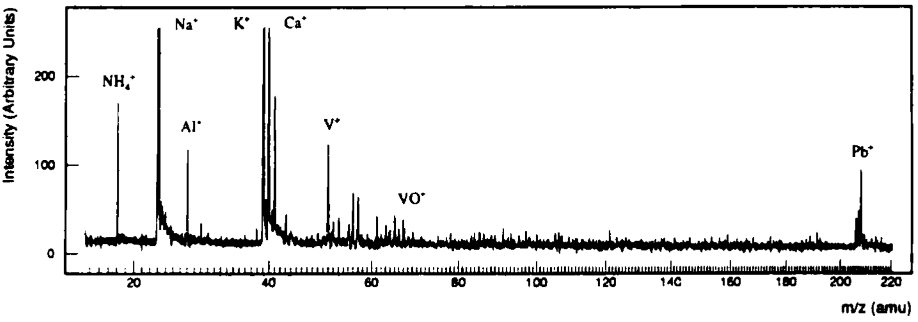

Figure 5 Positive mass spectrum of an ammonium-rich particle containing lead.

Detection of lead in natural aerosols

DPASV being a bulk analytical method, its results represent averages over a large amount of aerosol particles. In order to obtain more detailed information, it is useful to fractionate the aerosol particles. It is possible to collect aerosols in different size ranges[4,11], which means that for every range such a titration can be performed in order to get information about the location of lead(II) in the particles. This still has to be investigated. Localizing lead in natural aerosols was first attempted with LAMMA.

As our aims were set on the localization of lead, particularly positive mass spectra were recorded. The amount of lead-containing particles was limited. Aerosol samples were taken with a 50% impactor stage cut-off diameter of 0.1 and 0.9 μm. In the analysed Wageningen aerosol samples, 19% and 5% of the recorded mass spectra contained lead, respectively. For the Ede aerosol samples, the percentages of lead-containing mass spectra were 24 and 41, respectively. Lead is more often detected in samples from Ede, collected near the A12 highway than in samples from Wageningen. Most spectra recorded on lead-containing particles showed the presence of vanadium. This element is a typical fossil fuel (diesel) combustion product and as such it is often detected in automotive exhaust-related particles[5]. A high abundance of NH_4^+-containing particles was measured. Ammonium compounds are reported to be closely associated with metals such as vanadium and lead[5,10]. A representative example of a recorded mass spectrum containing Pb(I), V(I) and NH_4(I) is given in Figure 5.

Information on the counterion's identity can be inferred from mass spectra recorded in the negative ion mode. Nitrate peaks (NO_x^-) are often detected, probably due to the agricultural surroundings of the sampling sites. The negative ion mode spectra, derived from particles sampled at Wageningen, are dominated by the HSO_4^- ion (Figure 6). This could indicate a particle composition corresponding to NH_4HSO_4 or $(NH_4)_2 SO_4$[15]. Pb-containing NH_4^+-rich particles (Figure 5) are thought to be secondary reaction products of automotive exhausts whereby $Pb(NH_4)_2(SO_4)_2$ is formed through a reaction of lead halides with $(NH_4)_2SO_4$[1]. In spectra recorded from particles at Ede (Figure 7), several other sulphate derived peaks could be detected: S^-, SH^-, SO^-, SO_2^-,$(H)SO_3^-$,$(H)SO_4^-$, $CH_3SO_4^-$. Even in some positive ion mode spectra, sulphate-related peaks could be seen: $(NaHSO_4)Na^+$, $(H_2SO_4)K^+$, $(Na_2SO_4)Na^+$, $(Na_2SO_3)K^+$, $(Na_2SO_4)K^+$, $(K_2SO_4)Na^+$.

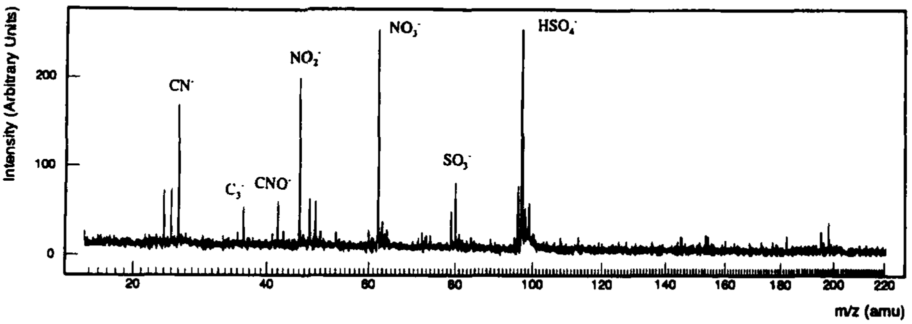

Figure 6 Negative mass spectrum of a sulphate- and nitrate-containing particle.

The results obtained illustrate once more that LAMMA is a suitable technique for the detection of lead in single particles. The detection limit for lead in 1 μm-diameter particles was reported to be 30 mg/kg^2, corresponding to an absolute detection limit of $4*10^{-17}$ g of Pb^{10}. Moreover, information regarding the aerosol-composition was obtained. The localization of lead, be it an inhomogeneous distribution as a surface coating or a homogeneous distribution, could, however, not be inferred.

CONCLUSIONS

Both DPASV and LAMMA are able to discriminate between Pb coated-and Pb-coprecipitated $CaCO_3$ standard particles. For natural, much more complex aerosols, no surface-related information could be obtained with LAMMA. This still has to be investigated with DPASV, but one will probably encounter the same difficulties. The complexity of the particles, as illustrated by the single-particle LAMMA measurements, poses the major limitation. The observed potential shifts in DPASV however, indicate that lead forms labile complexes with the chemical groups of aerosol particles.

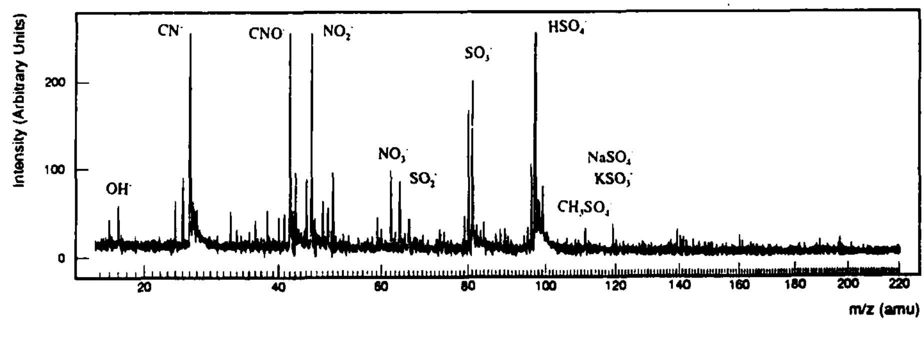

Figure 7 Negative mass spectrum of a sulphate- and nitrate-containing particle.

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