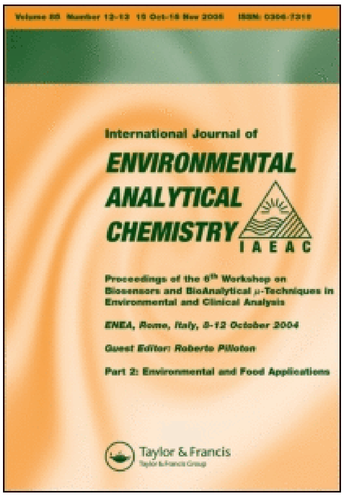

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Determination of Lead, Cadmium, Arsenic and Nickel in Atmospheric Particulate Matter by Simultaneous Multi-Element Electrothermal Atomic Absorption Spectrometry

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DETERMINATION OF LEAD, CADMIUM, ARSENIC AND NICKEL IN ATMOSPHERIC PARTICULATE MATTER BY SIMULTANEOUS MULTI-ELEMENT ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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A simple method for the determination of lead, cadmium, arsenic and nickel in atmospheric particulates by simultaneous multi-element Electrothermal Atomic Absorption Spectrometry has been developed. Due to the high concentrations of Pb and low concentrations of Cd, As and Ni found in particulate matter, lead was monitored at 261.4 nm and the other analytes at the usual wavelengths. Two approaches have been compared using aqueous standard solutions and acid extracts of particulate matter samples. First, a fast electrothermal programme, without chemical modifier, and a short pyrolysis step at 500°C for 10 s, has been developed. The omission of the pyrolysis step was not possible, because strong interference on arsenic was observed. The characteristic masses determined with this approach were 2.10 ng for Pb, 2.0 pg for Cd, 35.8 pg for As and 27.5 pg for Ni. The corresponding detection limits were 4.2 $\mu g\ l^{-1}$ (Pb), 0.025 $\mu g\ l^{-1}$ (Cd), 0.42 $\mu g\ l^{-1}$ (As) and 1.5 $\mu g\ l^{-1}$ (Ni), respectively. The second approach utilized the addition of Pd/Mg modifier (5 μg + 5 μg). The pyrolysis temperature (T_{pyr}) could be raised up to 650°C. The characteristic masses were 1.40 ng (Pb), 2.2 pg (Cd), 37.3 pg (As) and 27.9 pg (Ni). In the presence of Pd/Mg modifier the limits of detection were 4.3 $\mu g\ l^{-1}$ (Pb), 0.020 $\mu g\ l^{-1}$ (Cd), 0.26 $\mu g\ l^{-1}$ (As) and 0.97 $\mu g\ l^{-1}$ (Ni), respectively. These two approaches were applied in the determination of Pb, Cd, As and Ni in atmospheric particulates. Matrix matched calibration was used in order to achieve accurate and precise results. The calculated recoveries, in the absence of chemical modifiers, were 128% for Pb, 124% for Cd, 108% for As and 110% for Ni. The calculated recoveries were consistently better in the presence of the mixed Pd/Mg modifier: 101% (Pb), 99.7% (Cd), 103% (As) and 102% (Ni), respectively.

Keywords: Simultaneous Multi-element Electrothermal Atomic Absorption Spectrometry; lead; cadmium; arsenic; nickel; atmospheric particulate matter

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INTRODUCTION

European Commission legislation oblige member states to monitor the lead content in atmospheric particulates [1]. Recently, acknowledging that other metals in the air have detrimental effect on the human health, it was proposed that cadmium, arsenic, mercury and nickel should also be monitored in atmospheric particulates [2]. This proposal is expected to be adopted by member states soon. These two directives state that these elements should be determined in total suspended particulates (TSP) and propose Atomic Absorption Spectrometry as the reference method for these determinations.

Electrothermal atomic absorption spectrometry (ETAAS) is often used for the determination of the trace metal content in atmospheric particulate matter, due to its low detection limits, high selectivity and proven accuracy and it is the routine method for several laboratories [3]. However, its single-element nature is a severe drawback when the number of metals to be determined and the samples to be analyzed increase. This is the reason why XRF and ICP-based techniques remain dominant for multi-element analysis of atmospheric particulates [3]. However, with the introduction of new multi-elemental ETAAS systems [4–7], the analytical potential of this technique has increased. Transversely heated graphite atomizer (THGA), with its high atomization efficiency, provides efficient multi-element atomization conditions for analytes with varying volatility [8,9]. The combination of this atomizer with a high luminosity échelle grating polychromator in a tetrahedral configuration and a high quantum efficiency solid-state detector presents the state of the art of multi-elemental ETAAS [10,11].

The aim of this work was the development of a fast and reliable simultaneous multi-element ETAAS procedure for the determination of lead, cadmium, arsenic and nickel in atmospheric particulate matter. Since the concentration of lead is at least three orders of magnitude higher than the concentration of the other elements, its atomic absorption signal was recorded at a less sensitive, secondary line of 261.4 nm. Two approaches were compared: a fast temperature programme without the addition of any chemical modifier and a Pd/Mg modifier method. End-capped THGAs were also compared with the standard ones, since they provide improved sensitivity, reproducibility and detection limits [11–13].

EXPERIMENTAL

Instrumentation

The Perkin Elmer SIMAA 6000 spectrometer equipped with a THGA graphite furnace with longitudinal Zeeman-effect background correction and an AS-72 autosampler was used. For the simultaneous determination of Pb, As, Cd and Ni, the 4-element simultaneous mode of the spectrometer was used, using electrodeless discharge lamps (EDL2 System) for Pb (261.4 nm, 440 mA), Cd (228.5 nm, 175 mA) and As (193.7 nm, 380 mA) and hollow cathode lamps Intensitron® for Ni (232.0 nm, 25 mA). Due to the highly variable concentration levels in particulate matter (high concentrations of Pb, low concentrations of Cd, As and Ni), Pb was monitored at the secondary line of 261.4 nm and the other analytes at the usual wavelengths. Standard THGA and end-capped THGA were compared. A 20-μl volume of the standard or sample solutions and a 5-μl volume of the modifier solution were dispensed in the graphite tubes with the AS-72 autosampler. Hot injection at 100°C was used to shorten the drying steps. The graphite furnace programme is summarised in Table I. Because the temperature programme is common for all elements determined, the apparent atomization temperature (T_{at}) is dictated by the least volatile of the elements, nickel, which shows an optimum T_{at} of 2300°C.

TABLE I Temperature programme for the simultaneous determination of Pb, As, Cd and Ni in atmospheric particulate matter

Step	*Temperature (°C)*	*Ramp time (s)*	*Hold time (s)*	*Ar flow rate (mL min^{-1})*	*Read*
Drying 1	110	5	10	250	
Drying 2	130	10	15	250	
Pyrolysis	Various[a]	Various[a]	Various[a]	250	
Atomization	2300	0	5	0	ON
Cleaning	2450	1	3	250	

a. Various T_{pyr} are: 300°C for a ramp time of 10 s and a hold time of 20 s or 500°C for a ramp time of 5 s and a hold time of 5 s, in the absence of modifier and 650°C for a ramp time of 10 s and a hold time of 20 s, in the presence of Pd/Mg modifier

Reagents

All reagents used in this study were of analytical-reagent grade. All glass and polypropylene ware were kept in 10% v/v HNO_3 for at least one night and then rinsed with 1% v/v HNO_3 and subsequently with distilled water before use. The acids were of Suprapur grade (Merck, Germany). Lead, cadmium, arsenic and nickel standards were prepared by diluting 1000 mg l^{-1} stock solution of each analyte (Titrisol, Merck, Germany) with ultra pure water (MilliQ water, Millipore) and acidified to a final HNO_3 concentration of 1% v/v. Palladium nitrate and magnesium nitrate (Merck, Germany), at a concentration of 10 g l^{-1}, were used for the preparation of the modifier solution (final concentration 1 g l^{-1} for both elements).

Procedures

Optimization and comparison of the approaches

For the choice of the maximum permissible pyrolysis temperature (T_{pyr}), pyrolysis curves were constructed without and with the addition of the modifier solution. The calibration curves were constructed by injecting 20 μl of three multi-element standard solutions containing 0.5, 1.0 and 1.5 mg l^{-1} Pb, 0.5, 1.0 and 2.0 μg l^{-1} Cd, 10.0, 30.0 and 60.0 μg l^{-1} As and 30.0, 50 and 70.0 μg l^{-1} Ni, respectively, in the graphite tube and measuring integrated absorbance (A_i). The characteristic mass, m_0 (pg), was calculated from the slope (*b*) of the standard curve, using the equation $m_0 = 0.0044 \times 20/b$ for a sample volume of 20 μl. The limit of detection, LOD (μg l^{-1}), was calculated from the equation LOD $=3 \times S_{BL}/b$, where S_{BL} was the standard deviation of ten blank determinations.

Determination of Pb, Cd, As and Ni in atmospheric particulates

Atmospheric particulate matter samples were collected on a daily basis with high volume samplers (General Metal Works Inc.) on glass fiber filters. Therefore, the exact duration of air sample collection was 24 h. The flow rate was varied between 1.0 and 1.5 m^3 $min^{-1}$and it was recorded every day. A quarter of the filter was subjected to a HNO_3-HCl extraction in an ultrasonic bath at 50°C for 30 min [14]. The resulting solution was filtered and diluted to 50.0 ml with ultrapure water (MilliQ water, Millipore). A 20 μl volume of the sample was injected into the graphite tube with or without 5 μl of the modifier solution. The temperature programme given in Table I was followed. Pyrolysis curves were also constructed without and with the addition of the modifier solution, for the optimization of the temperature programme. Quantification was performed with matrix-matched calibration curves, constructed from integrated absorbance measurements and prepared by spiking the extract of a sample with the standard solutions mentioned under *Reagents*. Recoveries were calculated from the matrix-matched curves.

RESULTS AND DISCUSSION

Comparison of the two approaches

Optimization of the instrumental parameters

The content of lead in TSP is at least three orders of magnitude higher than the content of the other toxic elements. When one considers the simultaneous determination of Pb by ETAAS, along with Cd, As and Ni, should find a less sensitive line to monitor lead absorbance, in order to avoid dilutions of the sample. The SIMAA 6000 offers a choice of three wavelengths for Pb, the two sensitive, usual wavelengths (217.0 and 283.3 nm) and a less sensitive, secondary line at 261.4 nm. This wavelength is suitable for the determination of the lead content in atmospheric particulate matter, since the sensitivity is 25 times lower, as it was suggested in the literature [10].

After selecting the appropriate wavelengths, we tried to develop a fast programme, omitting the pyrolysis step and the use of chemical modifiers, in order to increase the sample throughput. It was proved that the omission of the pyrolysis step was not possible due to severe interferences on arsenic signal from the matrix of the sample. Therefore, a pyrolysis step was included in the final temperature programme of the THGA. When a temperature programme for simultaneous multi-element analysis by ETAAS is to be developed, compromise furnace temperatures have to be considered. The degree of compromise is related to the group of analytes to be determined. The maximum pyrolysis temperature (T_{pyr}) that could be applied was imposed by the most volatile element, which in this case was Cd with a T_{pyr} of 300°C in the absence of modifiers. It was found that the standard solution could be pyrolysed at 500°C for 10 s (5 s ramp time and 5 s hold time) without losses of Cd sensitivity. In the presence of the mixed Pd/Mg modifier, T_{pyr} could be raised up to 650°C without losses of Cd. In both cases, the atomization temperature (T_{at}) was 2300°C, dictated by the most refractory element, Ni. Hence, the compromise parameters are completely different than individually optimized single-element conditions. The transient signals of a mixed standard solution (0.5 mg l^{-1} of Pb, 1 $\mu g\ l^{-1}$ of Cd, 10 $\mu g\ l^{-1}$ of As and 30 $\mu g\ l^{-1}$of Ni) are shown in Figure 1 (without chemical modifiers) and Figure 2 (with Pd/Mg modifier). The AA profiles for all the elements are sharper in the presence of the mixed modifier, but the background absorbance is increased.

Analytical figures of merit

Calibration curves were constructed following the procedure described in the experimental session, and applying the temperature programme given in Table I. From the slope of the standard curves the sensitivity and limit of detection were calculated. End-capped THGAs were compared with the standard tubes. These results are summarized in Table II. It was found that the fast pyrolysis step at 500°C exhibits the same sensitivity and detection limit as the usual pyrolysis step at 300°C, hence only the results of the latter procedure are presented in Table II. The use of the multi-element T_{at} of 2300°C obviously causes a loss of sensitivity particularly for the volatile elements, Pb and Cd. With and without Pd/Mg modifier, the sensitivity loss for Cd is approximately 50–60%. This is in agreement

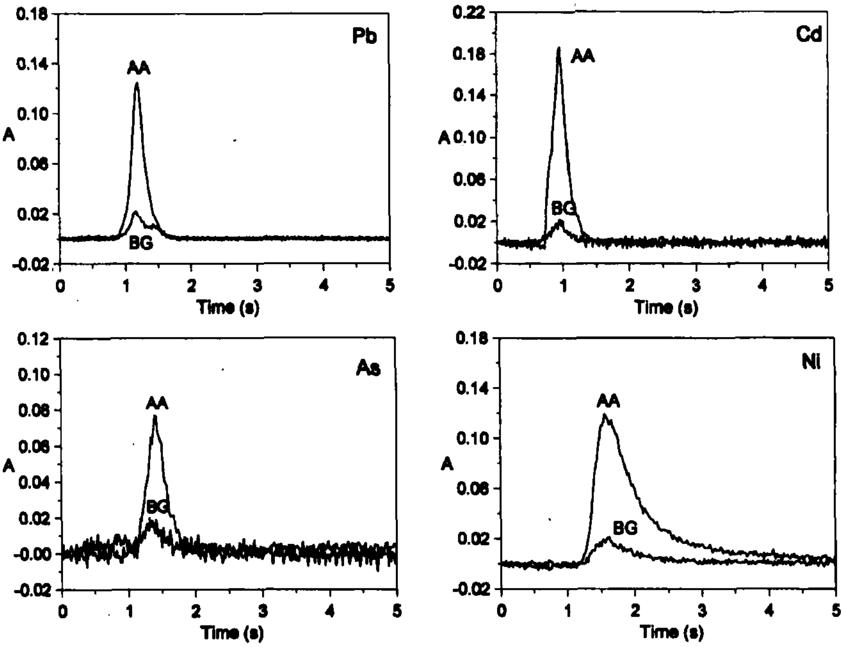

FIGURE 1 (AA) Atomic absorption and (BG) background absorption signals of Pb, Cd, As and Ni in aqueous samples, in the absence of chemical modifier. T_{pyr}=300°C and T_{at}=2300°C

with the theoretically predicted decrease if the dominant loss mechanism is diffusion, and is in line with previously reported results [8,9]. For As and Ni, the characteristic masses are not affected by the addition of Pd/Mg modifier and are approximately the same or even better with those given by Perkin-Elmer [15]. However, Pb sensitivity is increased by a factor of 1.5 with the addition of Pd/Mg. Perkin-Elmer suggests a characteristic mass of 60 pg with Pd/Mg modifier at the 283.3 nm and at four-element mode [15]. If one considers that Pb sensitivity at 261.4 nm is 25 times lower than that of the recommended wavelength of 283.3 nm [10], then the characteristic mass found in this study (1400±270 pg) is in agreement with the calculated one (1500 pg), in the presence of Pd/Mg modifier.

The use of end-capped tubes enhanced sensitivity by factors of 1.5 to 2.0 without modifier and by factors of 1.2 to 2.6 with the modifier. The greatest increase in sensitivity is observed for As. The enhancement in sensitivity is explained by the increased analyte residence times, since the reduced apertures of the end-capped THGA restrict the diffusional losses [8,9]. Another possible reason is that the analyte trapping by the matrix (chemical modifier or sample matrix) is

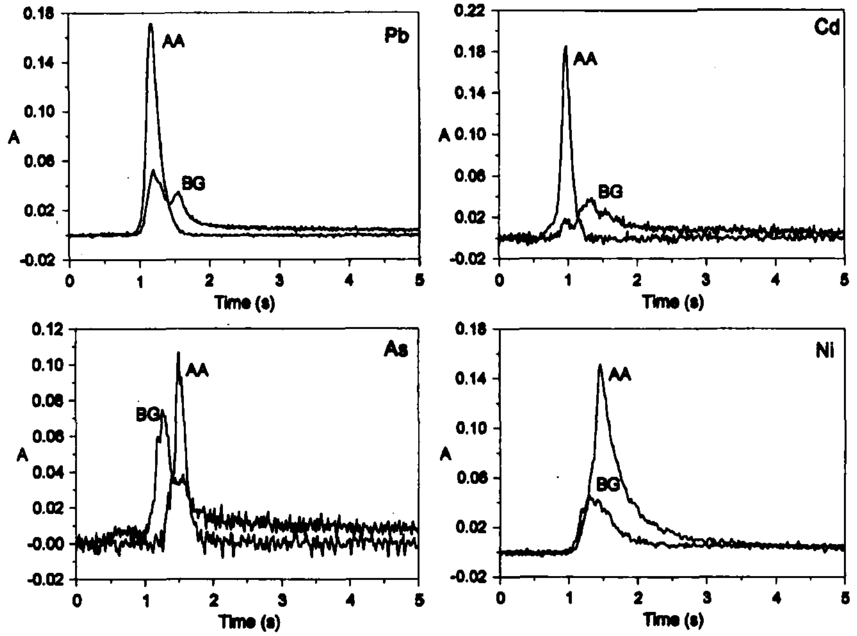

FIGURE 2 (AA) Atomic absorption and (BG) background absorption signals of Pb, Cd, As and Ni in aqueous samples, in the presence of Pd/Mg modifier. T_{pyr}=650°C and T_{at}=2300°C

diminished in the end-capped tubes [8]. The improved sensitivity of As and Pb in the presence of Pd/Mg modifier with end-capped tubes could be attributed to this fact.

TABLE II Analytical characteristics of the simultaneous determination of Pb, As, Cd and Ni using standard and end-capped THGA, in the presence and in the absence of Pd/Mg modifier

	Pb	*As*	*Cd*	*Ni*
Without modifier – std. THGA				
m_0 (pg) (n=5)	2100±220	35.8±3.1	2.0±0.2	27.5±1.5
LOD (μg l^{-1})	4.2	0.42	0.025	1.5
%RSD[a] (n=5)	5.7	5.2	1.6	3.8
Without modifier – end-capped THGA				
m_0 (pg) (n=3)	1400±230	18.2±1.5	1.2±0.1	16.9±0.2
LOD (μg l^{-1})	3.8	0.39	0.028	1.9
%RSD[a] (n=5)	3.4	5.0	1.2	2.7

	Pb	*As*	*Cd*	*Ni*
With Pd/Mg modifier – std. THGA				
m_0 (pg) (n=5)	1400±270	37.3±5.1	2.2±0.2	27.9±3.3
LOD (μg l^{-1})	4.3	0.26	0.020	0.97
%RSD[a] (n=5)	1.6	4.1	1.7	0.9
With Pd/Mg modifier – end-capped THGA				
m_0 (pg) (n=3)	1180±180	14.5±2.0	1.4±0.2	17.6±0.2
LOD (μg l^{-1})	2.9	0.30	0.025	0.85
%RSD[a] (n=5)	1.9	2.7	1.0	0.8

a. RSD (%) were calculated for the following concentrations: 0.5 mg l^{-1} Pb, 10 μg l^{-1} As, 1.0 μg l^{-1} Cd and 30 μg l^{-1} Ni.

Consequently, the limits of detection are similar with (As, Ni) or slightly worse (Cd) than those proposed by Perkin-Elmer [15]. Use of the end-capped tubes did not improve the LODs with or without modifier. The relative standard deviation is slightly better in the presence of Pd/Mg modifier, especially in combination with end-capped tubes, even though the background absorbance is increased in the presence of this modifier (Fig. 2). Nevertheless, the developed methodologies were applied in the determination of these analytes in acid extracts of atmospheric particulate matter.

Determination of Pb, Cd, As and Ni in TSP

The pyrolysis step was also optimized for the samples, in order to investigate possible matrix effects on the thermal stability of the analytes. The pyrolysis curves of Pb, Cd, As and Ni in an acid digests of particulate matter, without or with Pd/Mg modifier are shown in Figures 3 and 4. In the absence of chemical modifier, no extra thermal stabilization was observed by the sample matrix, except a small increase in T_{pyr} of As. Similarly, the sample could be pyrolysed at 500°C for 10 s (5 s ramp time and 5 s hold time) without losses of Cd sensitivity. The addition of Pd/Mg modifier improved thermal stability of the analytes, as it was expected. The AA signal of As and Ni were thermally stable up to 1300°C in the presence of Pd/Mg, but the compromise maximum T_{pyr} that it could be applied is 650°C, restricted by Cd. However, the background absorbance in the presence of this modifier is substantially increased. The longitudinal Zeeman background corrector can easily compensate for this absorbance, but the baseline noise is increased, affecting, consequently, the precision and the limits of detection.

In order to investigate the presence of matrix interference and exploit the possibility of performing calibration by simple aqueous solutions, calibration with

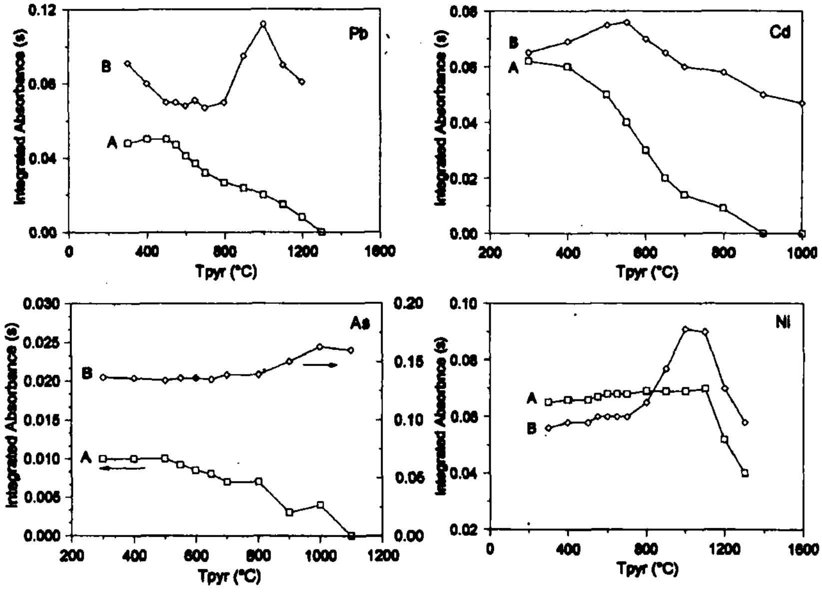

FIGURE 3 Effect of pyrolysis temperature (T_{pyr}) on (A) atomic absorption and (B) background absorption signals of Pb, Cd, As and Ni in acid digests of atmospheric particulates sample, in the absence of chemical modifier (a 10s ramp time and 20s hold time was used for the pyrolysis step; T_{at}=2300°C)

aqueous standards and with standard additions was performed. It was observed that, in the absence and in the presence of the modifier, the slopes of the calibration curve (SC) and the standard addition curve (SAC) are different for all the analytes, measuring both the peak height absorbance and the integrated absorbance (Table III). This means that calibration with matrix-matched standards should be applied for accurate results. The slopes of the standard addition curves without modifiers were always higher than those in the presence of Pd/Mg modifier. In order to check the accuracy of the proposed methods, recovery experiments were carried out with and without modifier and the results are summarized in Table IV. Consistently better recoveries were obtained in the presence of Pd/Mg modifier. Therefore, the determination of these elements should be carried out with the addition of the Pd/Mg modifier.

The limits of detection (LODs) and the relative standard deviations (RSDs) for the determination of Pb, Cd, As and Ni in atmospheric particulates are given in Table V. The LODs were calculated from the matrix-matched calibration curves as three times the standard deviation of ten replicate measurements of a blank filter. It can be noticed that LODs and RSDs were slightly higher in the presence of

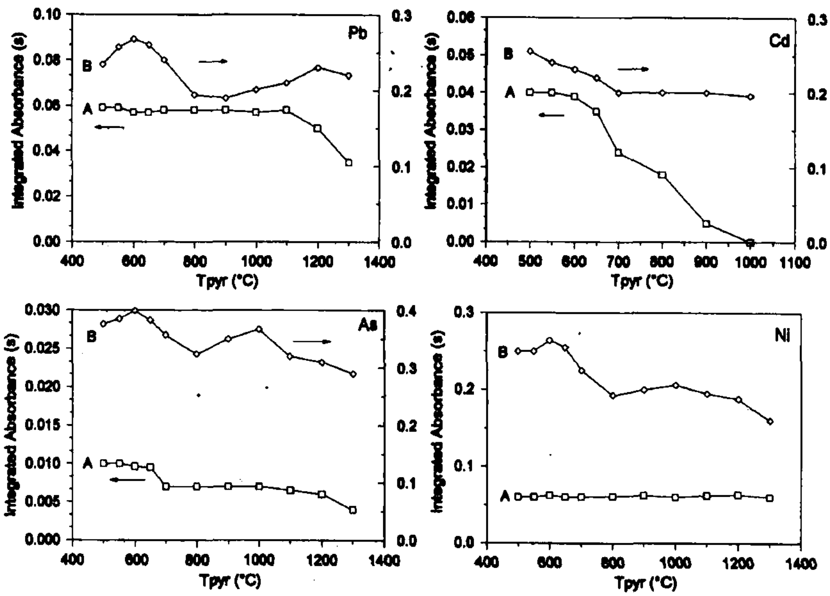

FIGURE 4 Effect of pyrolysis temperature (T_{pyr}) on (A) atomic absorption and (B) background absorption signals of Pb, Cd, As and Ni in acid digests of atmospheric particulates sample, in the presence of Pd/Mg modifier (a 10s ramp time and 20s hold time was used for the pyrolysis step; T_{at}=2300°C)

Pd/Mg modifier. This could be attributed to the increase of the background absorbance in the presence of this modifier, which in turn increases baseline noise. Nevertheless, the modifier method was applied to the simultaneous determination of Pb, Cd, As and Ni in TSP collected in an urban station in Athens. The concentrations found were typical for urban areas (Pb: 0.13±0.04 μg m^{-3}; Cd: 0.36±0.35 ng m^{-3}; As: 0.96±0.34 ng m^{-3}; Ni: 3.82±2.60 ng m^{-3}, n=20). Lead concentration was lower than the guideline of 0.5 μg m^{-3} [16]. The sample throughput was 24 h^{-1}, adequate for routine use in laboratories for environmental analysis.

TABLE III Comparison of the slope of calibration curves using aqueous standard solutions (SC) and the slope of matrix matched calibration curves (SAC) for the simultaneous determination of Pb, As, Cd and Ni in atmospheric particulate matter extracts

	Slope (s l μg^{-1})			
	Pb	*As*	*Cd*	*Ni*
Without modifier				
SC	32.4	0.0032	0.044	0.0032

	Slope (s l µg^{-1})			
	Pb	*As*	*Cd*	*Ni*
SAC	25.8	0.0027	0.032	0.0025
With Pd/Mg modifier				
SC	69.8	0.0026	0.040	0.0032
SAC	17.3	0.0012	0.017	0.0013

TABLE IV Recovery of Pb, As, Cd and Ni added to the acid extracts of particulate matter with and without Pd/Mg modifier

	Recovery (n=8) (%)	
	Without modifier	*With Pd/Mg modifier*
Pb	128±12	101±4
As	108±4	103±3
Cd	124±10	99.7±3.4
Ni	110±6	102±3

TABLE V Limits of detection (LOD, ng m^{-3}, n=10, k=3) and relative standard deviation (RSD, %, n=5) obtained for the simultaneous determination of Pb, Cd, As and Ni in atmospheric particulates

	Without chemical modifier		*With Pd/Mg modifier*	
	LOD (ng m^{-3})	*RSD^{a} (%)*	*LOD (ng m^{-3})*	*RSD^{a} (%)*
Pb	0.48	0.9	1.64	5.7
Cd	0.0033	1.5	0.0056	2.2
As	0.047	5.2	0.056	10
Ni	0.18	4.9	0.23	5.5

a. RSD (%) were calculated for the following concentrations: 0.14 µg m^{-3} Pb, 0.56 ng m^{-3} As, 0.12 ng m^{-3} Cd and 1.92 ng m^{-3} Ni.

CONCLUSIONS

The Pd/Mg method developed here for the simultaneous determination of Pb, Cd, As and Ni by ETAAS in atmospheric particulates is relatively rapid (24 samples h^{-1}) and the results are of acceptable quality. The SIMAA 6000 provides a less sensitive, secondary line for Pb (261.4 nm) which is adequate for its direct determination at high concentrations found in TSP, thus avoiding time-consuming and error-prone dilutions. However, matrix-matched calibration should be performed. Sensitivity and limits of detection are more than sufficient for the concentrations of these elements in atmospheric particulates. Low operating cost makes this technique ideal for monitoring purposes and low-budget laboratories, but also useful for quality control of the results, since modern ETAAS (THGAs, longitudinal Zeeman background correction, solid state detector) is a mature and well-tested technique. Simultaneous multi-element ETAAS is therefore a good alternative in terms of limits of detection, sensitivity, control of interferences and productivity to ICP-based techniques.

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