Analysis of heavy metals in atmospheric particulate by ion chromatography

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Abstract

Cu, Ni, Zn, Co, Fe^{+2}, Mn, Cd, Fe^{+3} and Pb are easily separated and detected in isocratic mode by ion chromatography with post-column derivatization using a bifunctional ion-exchange column and an eluent formed by oxalic acid (28 mM) and sodium nitrate (250 mM). The separation is optimised by using a suggested sample solution containing a given concentration of chloride. Detection limits were 10–15 ppb for all the metals except for cadmium and lead, for which detection limits of 30 and 60 ppb were found, respectively. The method was tested on an atmospheric particulate certified sample. The measured values were in good agreement with certified values. Real samples of atmospheric particulate from industrial and urban sites were analysed and the results are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently a paper was published [1] concerning the ion chromatography (IC) determination of Cu, Ni, Zn, Co, Mn, Cd, Pb, Fe^{+2} and Fe^{+3}. This method used a bifunctional ion-exchange column (CS5A Dionex, Sunnyvale, USA) exploiting the different net charges due to the different degrees of association between the metal and a chelating agent, in order to analyse heavy and transition metals in marine sediments. The quantitative determination was performed by spectrophotometry after post-column derivatization with a complexing dye. In particular, oxalic acid was used as the complexing agent and a gradient elution with two solutions containing the same concentrations of oxalic acid, hydrochloric acid,

sodium chloride and a different concentration of sodium nitrate was found suitable for optimising the separation. The above-mentioned method represents a very useful improvement in comparison with the previous elution procedures. In fact, a complete analysis of these transition and heavy metals involved the use of two different eluents based on oxalic acid [3] and PDCA (pyridine-2,6-dicarboxylate) [3,4], respectively. In fact, in the first method oxalic acid at pH 4.7 does not allow separation of Mn and Cd and iron determination while PDCA as the eluent does not allow the detection of lead by post-column reagents because of the strong stability of the PDCA complex. However, the gradient elution entails some problems since it can concentrate on the top of the column some metals that are contained in trace amounts in the weakest of eluent solutions; also, the time of analysis is increased because the column must be reconditioned to the initial con-

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ditions after each run. Lastly, not all the ionic chromatographs, particularly those present in the public surveillance labs, are equipped with gradient delivery systems. In this paper, we will show that complete resolution and quantification of the above considered cations can be obtained in isocratic mode in 10 min. Resolution was optimised by a suitable choice of co-electrolyte added to the sample solution. The effect of the eluent components concentration and the injected solution has been studied. We have also tested the detection limits and the reproducibility of the suggested method. The method has been applied on real samples of atmospheric particulate. Recovery tests and validation by analysing standard reference material have been performed.

2. Experimental

2.1. Instrumentation

A high pressure ion chromatograph (Dionex 4500i Sunnyvale, CA, USA) equipped with a PC10 post-column pneumatic controller and a spectrophotometric variable wavelength detector positioned at 530 nm was used. Introduction of the sample was performed by a pneumatic microinjection valve with a 200-μl injection loop. The analytical column was a 250×4 mm I.D. IonPac CS5A (Dionex, Sunnyvale, CA, USA) preceded by a guard column (50×4 mm I.D. IonPac CG5A by Dionex). The column outlet and the post-column reagent were conveyed, through a 3-way connector, to a 375-μl mixing coil followed by the detector cell. Particulate sample digestions were performed by a focused microwave wet digester (Microdigest 3.6 Prolabo, Fontenay, France) equipped with an aspiration module (Aspivap by Prolabo).

2.2. Reagents and standards

All reagents were analytical-grade. Trace select-ultra nitric acid (Fluka, Milwaukee, WI, USA), oxalic acid dihydrate (Fluka), sodium chloride (C. Erba, Milano, Italy), 4-(2-pyridylazo) resorcinol (PAR; Riedel de Haën, Milwaukee, WI, USA) and ammonium hydroxide (Sigma, Milwaukee, WI, USA) were employed. A stock standard solution containing

100 mg/l of each cation was prepared by atomic spectroscopy standard solutions (1000 mg/l, Fluka) and working standards were obtained by suitable dilution. Ultrapure water (Resistivity>18.2 MΩ cm) was produced by a Milli-Q system (Millipore, Bedford, MA, USA). Glasses were treated according to normal precautions for trace analysis.

2.3. Eluents and post-column reagent

A mixture of oxalic acid and sodium nitrate was employed as the eluent. The eluent concentration optimised for the best resolution was: oxalic acid (28 mM) and sodium nitrate (250 mM). A solution of PAR 0.12 mg/l in ammonium hydroxide (3 M) was used as a post-column reagent. Chromatographic conditions were as follows: injection column: 200 μl, guard column: IonPac CG5A, analytical column: IonPac CS5A, eluent: $C_2H_2O_4$ (28 mM), NaNO$_3$ (250 mM), eluent flow: 1 ml/min, detection: Vis λ=530 nm, post-column reagent: PAR (0.12 mg/l), NH$_4$OH (3 M), reaction coil: 375 μl and post-column reagent flow: 0.6 ml/min

2.4. Sampling and digestion of particulate matter

Atmospheric particulate was sampled by a portable constant air flow sampler (BRAVO M2, Corsico, MI, Italy) at a flow of 20 l/min on a polycarbonate 47-mm, 0.2-μm membrane (GTTP 04700 Millipore, Bedford, MA, USA) with a sampling time of 24 or 48 h. This membrane was chosen due to the very low release of heavy metals during the extraction step [5]. The particulate was extracted by digesting the membrane in a microwave wet-digester. In this apparatus a focused beam irradiates, with 2450 MHz microwaves, a volume portion of 40 ml of a 250-ml quartz flask. An IR sensor, connected with a digital-programming console which allows the setting of several multistep programs, controls the temperature inside the flask. After the digestion an Aspivap module dried the sample. The residue, containing the metals mainly in nitrate form, was dissolved in 10 ml of a mixture formed by sodium chloride, sodium nitrate and oxalic acid, filtered through an Autotop WF Plus 0.4-μm polycarbonate filter (Whatman, Maidstone, England) and injected in the chromatograph. The quantitative composition

of the dissolving mixture is very important to obtain a good resolution as discussed in Section 3.

3. Results and discussion

3.1. Optimisation of the chromatographic method

When heavy and transition metals are injected in the column and a chelating carboxylic acid is present in the eluent mobile phase complexation of the metals takes place. The degree of complexation and the molecular ratio between the metal ion and the carboxylic acid depend on the complexing constants, the ratio between the concentration of chelating agent and metal, the pH, the presence of other complexing anions like chloride and on the presence of other cations that can compete for the complexing agent. Metals can be present as hydrate metal ions with a positive charge or as complexes with a charge depending on the stoichiometry of the complex. IonPac CS5A has anionic and cationic sites so that both the free metals and the above mentioned complexes can be selectively retained. Carboxylic acids like oxalic, tartaric, citric, lactic or PDCA [1–9] have been used as complexing agents. However, the common eluents (oxalic acid or PDCA) do not allow the detection of iron and lead respectively due to the strong stability of their complexes with bicarboxylic acids at typical eluents pH values. Other methods to obtain a complete separation and determination of heavy and transition metals in isocratic mode, also using other kind of columns, were suggested, but no author showed the simultaneous detection of iron and lead. Cardellicchio et al. [1], by using a gradient mode for elution, obtained a satisfactory separation of these elements. Our aim is to obtain the same results using an isocratic mode reducing the analysis time and the disadvantages [2] concerning the gradient mode in this way. We have therefore carried out a series of experiments by changing the parameters of the analysis by using oxalic acid as the complexing agent. Cardellicchio et al. showed that using oxalic acid as the eluent at pH~1.3 all the above mentioned metals, except lead, were eluted while a concentration 265 mM sodium nitrate was necessary to elute lead. However, in the presence of chloride >5 mM this concentration of
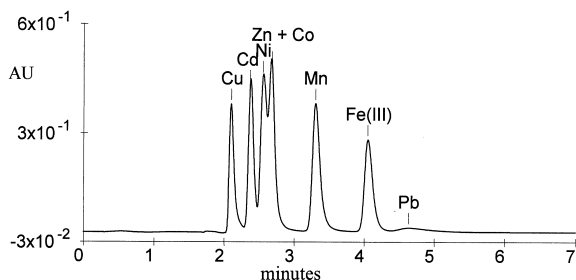

Fig. 1. Chromatogram of a heavy metals standard (500 ppb) injection with an eluent containing oxalic acid (28 mM), sodium chloride (50 mM) and sodium nitrate (265 mM).

nitrate lead to a worse separation between Cd, Ni, Zn and Co (Fig. 1).

An attempt to improve the resolution by decreasing the pH did not significantly improve the separation and increased the analysis time due to the lower eluent power. The increase of the oxalic acid concentration up to 50 mM worsened the resolution.

The use of an eluent with 28 mM oxalic acid and 265 mM sodium nitrate produce a good resolution between the peaks (Fig. 2).

For all these experiments, the injected solution was obtained by diluting standard stock solution with the eluent. We obtained a satisfactory separation by eliminating chloride from the eluent and adding it to the sample; in fact, when 50 mM chloride was added to the sample we had a good separation coupled with a significant increase of the signal (Fig. 3). Besides, since the ionic strength of this solvent sample is very close to the eluent one, the negative counter peak at the beginning of the chromatogram was minimised.

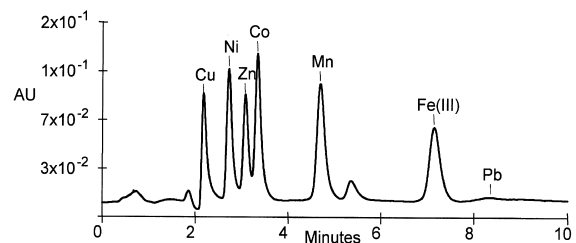In conclusion, the optimised conditions were eluent: 28 mM oxalic acid and 250 mM sodium

Fig. 2. Chromatogram of a heavy metals standard (200 ppb) injection with an eluent containing oxalic acid (28 mM) and sodium nitrate (250 mM).
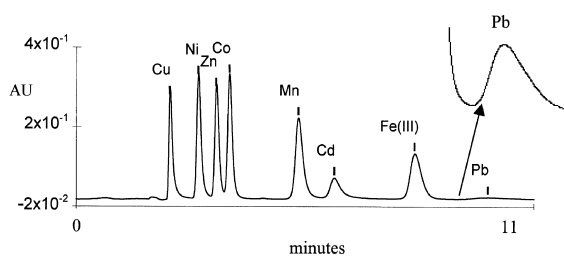
Fig. 3. Chromatogram of a heavy metals standard (500 ppb) in sample solution with an eluent containing oxalic acid (28 mM) and sodium nitrate (250 mM).

Table 1
Limit of detection (LOD) and limit of quantification (LOQ) for chromatographic method

Elements	LOD (ppb)	LOQ (ppb)
Pb	60	200
Fe	15	50
Cu	10	30
Co	10	30
Cd	30	100
Ni	10	30
Mn	10	30
Zn	10	30

nitrate; sample solution: 28 mM oxalic acid, 120 mM sodium nitrate and 50 mM sodium chloride.

Under these conditions the column works practically in a sort of gradient since the injected volume is a significant portion of the total volume of the mobile phase. Moreover, the suggested chromatographic method allows a speciation of Iron, since Fe^{+2} elutes between Co^{+2} and Mn^{+2} with very good resolution in a large range of pH.

3.2. Interferences and detection limits

When heavy and transition metals are analysed in real samples, the sample is usually acid digested, dried and dissolved again in acid solution (usually nitric acid, at pH<1). In this case a complete separation and detection of the analytes, because of the difference between the eluent pH and the sample one, are difficult when several metals are present in the sample for the above mentioned reasons. This inconvenient can be overcome by dissolving the dried residue in the suggested sample solution. A chloride concentration in the sample greater than 75 mM decreases the resolution of the peaks and in particular the resolution between Mn and Cd. Likewise, a nitrate concentration greater than 200 mM worsens the separation of the less retained metal peaks. A large amount of calcium produces a broad peak on the descending portion of Fe^{3+}; typically, 0.2 g/l calcium does not interfere with the quantification of 50 ppb of Fe^{3+}. In Table 1 the detection and quantification limits are presented. The limits of detection (LOD) and limits of quantification (LOQ) are defined as the concentrations showing a standard deviation which is respectively 1/3 and 1/10 of the relative signals.

3.3. Digestion and extraction tests

The particulate sample attack was performed by nitric acid in a focused microwave digester [5]. After drying, the residue was dissolved using the sample solution as described previously. The solution was filtered through an Autotop WF Plus 0.4-μm polycarbonate filter before injection. The recovery percentages have been tested using surrogated samples by spiking known quantities of standard metals in the concentration range of the real samples. The results are reported in Table 2.

One can see that a recovery of at least 70% with a standard deviation of less than 10% was obtained for the lowest concentrations. Both recovery and reproducibility were improved by increasing the amount of metal. For testing the proposed method certified standard reference materials [10] were analysed. In this case 100 mg of sample were taken since this is the minimum quantity related to the certified values [10]. As this quantity is about five times higher than the quantity of particulate usually sampled, the digestion procedure was slightly modified using 30 ml of nitric acid during the digestion step and drying only a portion of the digested sample. A calibration curve was built by submitting the standard metal solutions to the same procedure. The results relative to the duplicated certified sample analysis are reported in Table 3.

3.4. Atmospheric particulate analysis

We have carried out some sampling and relative analysis of urban and industrial atmospheric particulate in two streets of the Bari urban centre (Corso

Table 2
Percent of recovery for each metal in its concentration range[a]

Elements	Amount (μg)							
	0.5	0.7	1	2	5	10	30	40
Cu		80(5)	88(2)	92(2)				
Ni	80(6)		83(4)	92(3)				
Zn			75(7)		91(4)	95(2)		
Co	76(6)		82(4)		92(1)			
Cd		76(6)	82(5)	91(2)				
Fe						89(4)	93(3)	97(3)
Pb				85(5)	88(3)	95(2)		

[a] Number in brackets represents the standard deviation on triplicate measurements.

Table 3
Comparison between measured and certified concentrations of Standard Reference Material 1648

Elements	Measured values (g/Kg)	Certified values (g/Kg)
Cu	0.577±0.038	0.609±0.027
Ni	0.082±0.008	0.082±0.003
Zn	4.500±0.300	4.760±0.140
Mn	0.750±0.038	0.786±0.017
Fe	32.000±3.000	39.100±1.000
Pb	6.200±0.400	6.550±0.080

Cavour, Via Amendola, Italy) and in a site confining the Taranto industrial area (Rione Tamburi, Italy). The chromatogram relative to an urban sample is shown in Fig. 4.

The results are reported in Table 4. The uncertainties on the measurements depend essentially on the digestion reproducibility. The detection limits referred to particulate, as reported in Table 5, are calculated for a sampling time of 24 h and a flow of 20 l/min taking into account Table 2 and the blank analysis uncertainties.
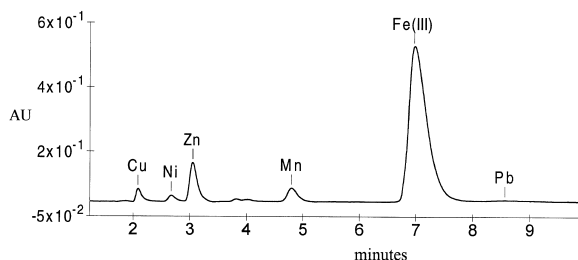
Calibration curves for particulate analysis were

Fig. 4. Via Amendola sample (10/20/99) chromatogram.

obtained by spotting known amounts of a stock metal solution of polycarbonate membranes and then carrying out the whole procedure.

Inspecting Table 4 one can note:

1. An iron concentration in the industrial sample higher than in urban one. This is justified by the presence of a group of metal industries in the vicinity of the sampling site.
2. The presence of cobalt only in the industrial samples.
3. A lead concentration in the urban sample greater than the industrial one, but in any case this is not particularly relevant due to the introduction of unleaded fuels for motor transport.
4. A cadmium concentration under the detection limit and on the other hand a significant presence of nickel in the industrial samples. Both cadmium and nickel are considered harmful for their carcinogenic effects [11,12].

4. Conclusion

Heavy and transition metals, normally present in atmospheric particulate, can be separated and detected in isocratic mode by ion chromatography with a post-column reaction and spectrophotometric detection. For the separation, a bifunctional ion-exchange column and an eluent formed by oxalic acid and sodium nitrate are required. A very good resolution can be obtained by diluting or dissolving the sample in a solution with a composition very similar to the eluent one modified by adding a given concentration of chloride. The proposed pro-

Table 4
Concentration (μg/m^3) of heavy metals in industrial and urban samples of atmospheric particulate

Elements	Sampling site and date				
	Industrial site		Urban site		
	Rione Tamburi (9/29/99)[a]	Rione Tamburi (10/1/99)[b]	Corso Cavour (2/20/99)[a]	Corso Cavour (2/22/99)[a]	Via Amendola (10/20/99)[b]
Pb	0.10±0.02	0.25±0.02	0.30±0.08	0.40±0.08	0.280±0.040
Fe	1.80±0.10	2.42±0.06	0.80±0.06	0.91±0.07	0.750±0.030
Cu	0.33±0.07	0.30±0.04	0.33±0.07	0.46±0.08	0.310±0.030
Co	0.10±0.03	0.12±0.03	<0.01	<0.01	<0.005
Cd	<0.02	<0.01	<0.02	<0.02	<0.010
Ni	0.30±0.09	0.25±0.06	0.03±0.01	0.02±0.01	0.020±0.005
Mn	0.70±0.05	1.70±0.05	0.03±0.01	0.05±0.02	0.032±0.006
Zn	0.30±0.10	0.60±0.10	0.30±0.10	0.50±0.10	0.500±0.050

[a] Sampling time=24 h.
[b] Sampling time=48 h.

Table 5
Limit of detection (LOD) for entire proposed procedure

Elements	LOD (μg/m^3)
Pb	0.030
Fe	0.007
Cu	0.006
Co	0.010
Cd	0.020
Ni	0.006
Mn	0.006
Zn	0.010

cedure is particularly suitable in all types of analysis in which an acid attack of the sample is necessary. A test using certified standard material of atmospheric particulate gave values in good agreement with certified ones. Sensitivities are high for all metals except for lead that presents a detection limit of 60 ppb, however, this value is perfectly compatible with the lead concentration usually present in atmospheric particulate. We are actually engaged in improving the lead sensitivity testing new post-column reagents.

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