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Determination of heavy metals in air particulate matter by ion chromatography

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Abstract

In recent years, ion chromatography has been increasingly used for the separation and determination of heavy metals. In this study, the separation of Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} and Fe^{2+} in airborne particulate samples was achieved by the use of a complexing eluent containing 20 mM oxalic acid and 20 mM citric acid adjusted to pH 3.6 with lithium hydroxide. Upon elution, the separated metal ions were reacted with 4-(2-pyridylazo)resorcinol to form coloured complexes in a postcolumn reactor and detected by using a UV-Vis detector at 520 nm. The calibration graphs for the metal ions were linear in the range 1.0–3.0 $\mu\text{g}/\text{ml}$ for Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} , 8.0–24.0 $\mu\text{g}/\text{ml}$ for Pb^{2+} and 2.0–6.0 $\mu\text{g}/\text{ml}$ for Fe^{2+} . Detection limits for a 25- μl sample solution were 2.2, 0.9, 6.6, 0.9, 1.8 and 2.1 $\mu\text{g}/\text{l}$ for Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} and Fe^{2+} , respectively. The technique was optimized and validated by analysing the NIST standard reference materials SRM 1648 Urban Particulate Matter and SRM 1633b Coal Fly Ash.

Keywords: Air analysis; Environmental analysis; Derivatization, LC; Metal ions; Heavy metals; Pyridylazoresorcinol

1. Introduction

Ion chromatography, despite of being popular for the determination of anions and cations, was not widely used for the determination of heavy metals in the past, mainly owing to the incompatibility between the solvent for metals used in the dissolution of the samples of interest (normally in aqueous acidic conditions) and the hardware of the liquid chromatographic systems, and also the lack of a suitable detection system for heavy metals. However, rapid developments in separation columns and detection technology

in the last few years have opened up opportunities for the effective separation and detection of heavy metals in various media [1,2]. It has been possible to separate heavy metal ions by both reversed-phase and normal-phase chromatographic techniques [3] and by ion-exchange chromatography [1,4]. In the ion-exchange technique the metal ions are normally reacted with an anion of a weak organic acid to reduce their charge densities in the eluent solution before entering the separation column, where they are differentiated and separated based on their respective affinities towards the active sites of the separating resin [5–7].

This study was undertaken to investigate the

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applicability of ion chromatography to the determination of heavy metals (i.e., Cu, Cd, Co, Pb, Zn, Ni and Fe) in air particulate samples collected in an industrialized area. The technique was optimized and validated by analysing NIST standard reference materials (SRM) of a similar nature. The effect of sample dissolution procedures involving the use of direct heating with a hot-plate, a microwave oven and ultrasonication on the technique was also investigated.

2. Experimental

2.1. Chemicals

All the chemicals used, including lithium hydroxide monohydrate, oxalic acid dihydrate, citric acid, glacial acetic acid, nitric acid (65%), sulphuric acid (95–97%) and 4-(2-pyridilazo) resorcinol (PAR), were obtained from Merck (Darmstadt, Germany). Analytical-reagent grade ammonia solution was obtained from BDH (Poole, UK). SRM 1633b Coal Fly Ash and SRM 1648 Urban Particulate Matter were obtained from the National Institute of Standards and Technology (NIST), (Gaithersburg, MD, USA). Metal standard solutions were prepared by weighing and dissolving appropriate amounts of the metal salts in distilled deionized water, to make 1000 $\mu\text{g}/\text{l}$ stock standard solutions, which were preserved by adding 0.1–0.4 ml of HNO_3 . Lithium hydroxide was used throughout for the adjustment of the eluent pH in the ion chromatography of heavy metals ions.

2.2. Equipment

A Dionex Dx-300 high-performance ion chromatography equipped with a UV-Vis detector set at 520 nm was utilized. A 25- μl injection loop was used throughout. An IonPac CS2 column containing polystyrene packing with cross-linked divinylbenzene (DVB) with 2% sulphonyl functional groups covering the surface was obtained from Dionex. This column was operated in conjunction with an IonPac CG2 guard column. An MDS Model 81 microwave oven was used to

digest the SRMs at 630 ± 70 W with about 1% increments. A Milton Roy Spectronic 3000 Array spectrophotometer was used to determine the maximum peaks for the metal-PAR complexes. This spectrophotometer was connected to a Hewlett-Packard ColorPro plotter. A PE 5000 atomic absorption spectrophotometer equipped with a PE 500 graphite furnace (Perkin-Elwes) was used for the analysis of air particulate samples.

2.3. Acid digestion of the standard reference materials (SRM)

Extraction of the heavy metals from the SRMs were carried out by three different techniques: (a) direct heating on a hot-plate, (b) heating in a microwave oven and (c) ultrasonication.

The dissolution of the samples by the hot-plate acid extraction method was carried out according to Senger [8]. Approximately 0.100 g of the SRM was accurately weighed and placed in a 100-ml beaker, 15 ml of concentrated HNO_3 were added and the mixture was heated at about 140°C to near dryness. The sample was then filtered off using a 0.45- μm glass-fibre filter medium and rinsing the beaker with 10% HNO_3 . The solution was then heated again to near dryness. About 20 ml of 10% HNO_3 were added and the sample was allowed to cool to room temperature, then transferred into a 50-ml volumetric flask and diluted to volume with 10% HNO_3 .

Sample extraction using a microwave oven was carried out according to Bettinelli et al. [9]. A 0.100-g SRM sample was placed in 120-ml PTFE container and treated with HF-aqua regia- H_3BO_3 (5 + 15 + 6 ml). The sample was heated according to the programme shown in Table 1.

Table 1
Microwave open heating programme for the acid extraction of standard reference materials and air particulate samples

Step	Time (min)	Power (%)
1	8	50
2	4	80
3	7	50

After digestion was completed, the samples were transferred into 100-ml volumetric flasks and diluted to volume with 10% HNO₃.

Acid extraction by ultrasonication was carried out according to Ref. [10]. A 0.100-g SRM sample was placed in a 50-ml beaker, aqua regia (15 ml) was added and the beaker was covered with Parafilm to avoid spillage or contamination, then sonicated for 30 min. The beaker wall was rinsed with water and the washing were combined with the supernatant. The supernatant was transferred into a 50-ml volumetric flask and 20 ml of distilled water were added. The solution was shaken thoroughly, allowed to settle for 5 min, then diluted to volume with distilled water.

2.4. Air particulate sampling and sample preparation

Air particulate samples were collected from the Pasir Gudang Industrial Estate, Johor, Malaysia, in September–October 1993. A standard high-volume sampler was used for air particulate sampling. The sampler was operated daily (24 h) with a sampling flow-rate of 70 m³/h. A glass-fibre filter with an effective collecting area of 18 × 22.5 cm was used as the collecting medium. A portion (4 × 17.5 cm) of the filter sample was cut into small pieces with stainless steel scissors before being subjected to the different digestion procedures described above.

3. Results and discussion

3.1. Optimization of separation of metal ions

Separation of the heavy metal ions on the sulphonyl resin cation exchanger requires that the metal ions are complexed to reduce their charge density [11]. This improves the selectivity of the metal ions towards the active sites. Weak organic acids, such as oxalic, citric and tartaric acid, are normally used as complexing agents. In this study, a mixture of oxalic acid and citric acid was used as the eluent to separate the metal ions on the IonPac CS2 column. As expected, the concentration of the acids influenced the separation

of the metal ions. Therefore, the effect of the oxalic and the citric acid concentrations on the separation of the metal ions was studied and optimized. It was found that when the oxalic acid concentration was increased, the retention times of the metal ions were reduced (retention time was defined as the time between the injection of the sample and the peak maximum). For example, when 35 mM oxalic acid was used the metal ions were eluted within 10 min but they were poorly resolved and overlapped. On the other hand, when the oxalic acid concentration was reduced to 5 mM the retention time was about 40 min. An optimum separation of Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Pb²⁺ and Fe²⁺ was obtained by using an eluent mixture of 20 mM oxalic acid and 20 mM citric acid at pH 3.6 (Fig. 1A). However, under these conditions Fe³⁺ was not separated, probably because it forms a strong Fe(Ox)³⁻ complex [12].

The use of a secondary complexing agent often improves the separation performance of ion chromatography for heavy metals. In this study, it was found that an increase in the citric acid concentration reduces the retention times of the metals. When the oxalic acid concentration was about 20 mM, the optimum concentration of the citric acid was in the range 20–25 mM.

It was found that the separation of the metal ions using a weak acid eluent was susceptible to pH changes. For a given eluent strength, an increase in pH resulted in poor separation of the metal ions, i.e., a reduction in retention times and overlapping of the peaks. This was probably due to the increase in the concentration of the complexing ligand which reduced the affinity of the metal ions towards the cation-exchange sites of the resin. In contrast, when the pH was reduced, the peaks were more resolved and the retention times increased. Under low pH conditions the effective concentration of the ligand was reduced and the metal ions were held more strongly by the ion-exchange resin.

3.2. Optimization of detection of metals ions

PAR is generally the most suitable coloured complexant for the detection of heavy metals in

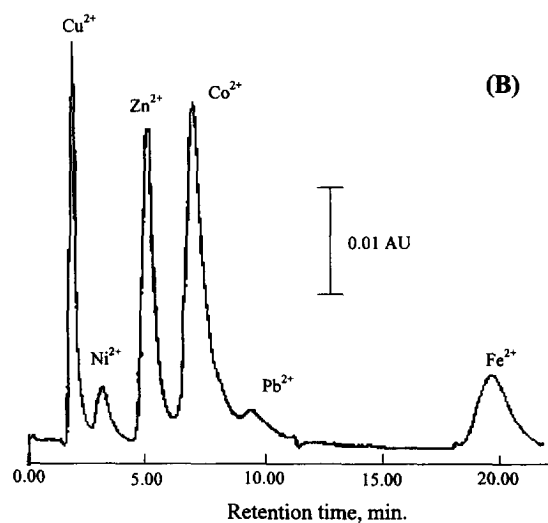
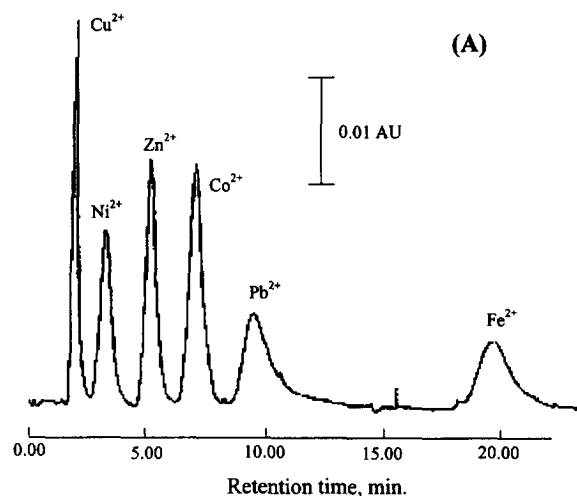


Fig. 1. Chromatogram of Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} ($1.0 \mu\text{g/ml}$), Pb^{2+} ($8.0 \mu\text{g/ml}$) and Fe^{2+} ($2.0 \mu\text{g/ml}$) on an IonPac CS2 column. Conditions: eluent, 20 mM oxalate– 20 mM citrate (pH 3.6) at flow-rate 1.0 ml/min ; postcolumn reagent, 0.2 mM PAR in 1 M ammonium acetate buffer (pH 9.0), measured at 520 nm , with PAR flow-rate (A) 0.7 and (B) 0.4 ml/min .

UV–Vis spectrophotometry [13]. In this study, the UV–Vis spectra of the PAR complexes with Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} and Fe^{2+} were recorded in ammonium acetate buffer (pH 9.0). The molar absorptivities of these metals at the λ_{max} and 520 nm are given in Table 2. Since the

Table 2

Molar absorptivity of the metal–PAR complexes at λ_{max} and 520 nm recorded in ammonium acetate buffer (pH 9.0)

Metal–PAR complex	λ_{max} (nm) ^a	Molar absorptivity ($\text{l/mol} \cdot \text{cm}$)	
		λ_{max}	520 nm
Pb	520	12210	12210
Co	510	63113	65979
Cd	500	8332	7769
Zn	495	50110	56701
Cu	500	57123	55778
Ni	490	49177	43709

^a λ_{max} is the wavelength at which molar absorptivity is maximum.

detector was normally set to operate at 520 nm , the values of the molar absorptivity at this wavelength indicate the relative sensitivities of the detector towards these metal ions. The data in Table 2 indicate that the relative sensitivities of these metal ions decrease in the order $\text{Co}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$. It was also found that PAR concentrations of less than 0.2 mM decreased the peak height. Higher concentrations of PAR may be used without a decrease in peak height, but it is not recommended for economic reasons.

Ammonium acetate buffer was used to maintain the pH of the postcolumn reaction at ≥ 9 to ensure the completion of complex formation. With a PAR concentration of 0.2 mM the peak height responses were optimized when the acetic acid and the ammonia concentrations were 1.0 and 1.5 M , respectively. At ammonia concentrations below 1.0 M the peak heights of Cu^{2+} , Co^{2+} and Zn^{2+} were severely reduced. Reductions in the peak heights of these metal ions and Ni^{2+} were also apparent when the ammonia concentration was greater than 2.0 M . It was found that the postcolumn reagent (PCR) flow-rate also affected the response of the eluted heavy metal ions. Under the conditions used, the optimum eluent flow-rate was 1.0 ml/min while that of the PCR was 0.7 ml/min (Fig. 1A). When the PCR flow-rate was lowered to 0.4 ml/min , the peak heights of Pb^{2+} and Ni^{2+} were severely

reduced (Fig. 1B). The following optimum conditions for the separation and detection of the metal ions were established and used in subsequent work: eluent, 20 mM oxalic acid–20 mM citric acid (pH 3.6, adjusted with LiOH) at a flow-rate of 1.0 ml/min; postcolumn detection with 0.2 mM PAR in 1.0 mM ammonium acetate buffer at a flow-rate of 0.7 ml/min.

Under the optimized conditions, the calibration graphs for the metals ions were linear in the range 1.0–3.0 $\mu\text{g/ml}$ for Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} , 8.0–24.0 $\mu\text{g/ml}$ for Pb^{2+} and 2.0–6.0 $\mu\text{g/ml}$ for Fe^{2+} . Generally, the linear correlation coefficients were better than 0.995. The detection limit was defined according to IUPAC and the ACS [14]. Since the technique was developed for the determination of metals in air particulate samples that were collected on glass-fibre filters, the results obtained for the blank filters were used as the “blank” in the calculation of the detection limits. By taking the detection limits as three times the standard deviation of the blank, it was found that for a 25- μl sample solution the detection limits were 2.2, 0.9, 6.6, 0.9, 1.8 and 2.1 $\mu\text{g/l}$ for Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} and Fe^{2+} , respectively.

3.3. Analysis of standard reference materials

As a validation of the analytical technique, two samples of standard reference materials of similar nature to the air particulate samples were analysed, NIST SRM 1633b Coal Fly Ash and SRM 1648 Urban Particulate Matter. They were subjected to the different acid extraction techniques, i.e., direct hot-plate heating, a microwave oven heating programme and ultrasonication and the results obtained are given in Table 3. Generally, it was found that the microwave oven method gave best recoveries. This was confirmed by the *t*-test statistics with 5% confidence levels which indicated that the recoveries of all metals were acceptable except for Fe^{2+} . With the exception of Co^{2+} and Fe^{2+} , it was apparent that the microwave technique gave satisfactory recoveries (70–100%). Nevertheless, for SRM 1648 Urban Particulate Matter the recovery for Co^{2+} was 77%, which was better than those with the hot-

plate and the ultrasonication techniques. The recovery of Fe^{2+} was consistently low for both samples, which could be due to the predominant oxidized state of the metal ions in the samples.

3.4. Analysis of air particulate samples

In addition to the total suspended particulate (i.e., particulate samples collected with the standard high-volume sampler), PM10 respirable particulate samples (i.e., particles with a diameter of less than 10 μm , as collected with a size-selective high-volume sampler) were also analysed. Both particulate samples were subjected to the same digestion procedures and analyses as for the SRM samples. It was found that the microwave oven technique gave better results than ultrasonication but comparable results to the direct hot-plate technique for both particulate samples.

The results of the heavy metals analysis by ion chromatography were compared with those obtained by AAS, which is a widely used method for the determination of heavy metals. Table 4 presents the results of the analyses with the *F*-distribution statistics for the two types of particulate samples analysed, which indicate that the results obtained by ion chromatography did not differ significantly from the AAS results except for iron. Since ion chromatography only detects Fe^{2+} whereas AAS measures total iron, the significant difference might indicate the nature of the elemental states in the air particulate samples.

4. Conclusion

It is evident from this work that ion chromatography with an IonPac CS2 column containing sulphonyl groups can be used for the rapid and accurate determination of heavy metals in air particulate samples. With a suitable combination of complexing agents such as oxalate and citrate, Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} and Fe^{2+} can be separated satisfactorily and detected by UV-Vis spectrophotometry after reaction with PAR. The calibration graphs for these metal ions were

Table 3
Analysis of SRMs by ion chromatography with IonPac CS2 column

Sample	Element	Amount found ^a and recovery (%)			Certified value ^a
		Hot-plate	Microwave oven	Ultrasonication	
SRM 1633 Coal Fly Ash	Cu ²⁺	640 ± 2 (105%)	580 ± 25 (95%)	228 ± 33 (37%)	609 ± 27
	Ni ²⁺	ND ^b (0%)	65 ± 15 (79%)	47 ± 0.5 (57%)	82 ± 3.0
	Co ²⁺	ND (0%)	8 ± 3 (44%)	1.25 ± 0.51 (7%)	18
	Zn ²⁺	0.464 ± 0.081 (98%)	0.399 ± 0.125 (98%)	0.154 ± 0.031 (32%)	0.476 ± 0.014
	Pb ²⁺	0.612 ± 0.051 (93%)	0.623 ± 0.033 (95%)	0.157 ± 0.021 (24%)	0.655 ± 0.008
	Fe ²⁺	1.99 ± 0.23 (51%)	2.06 ± 0.54 (53%)	2.45 ± 0.23 (63%)	3.91 ± 0.10
SRM 1648 Urban Particulate Matter	Cu ²⁺	100.7 ± 2.8 (89%)	122.2 ± 12.2 (108%)	85.47 ± 7.8 (75%)	112.8 ± 2.6
	Ni ²⁺	55.2 ± 5.3 (46%)	85.7 ± 25.3 (71%)	ND (0%)	120.6 ± 1.8
	Co ²⁺	27 ± 5 (54%)	38 ± 8 (77%)	4 ± 3 (8%)	50
	Zn ²⁺	175 ± 12 (84%)	170 ± 27 (81%)	114 ± 11 (54%)	210
	Pb ²⁺	47.1 ± 1.1 (69%)	58.3 ± 9.6 (86%)	35.1 ± 0.8 (52%)	68.2 ± 1.1
	Fe ²⁺	2.88 ± 1.11 (37%)	4.89 ± 1.11 (63%)	1.45 ± 0.33 (19%)	7.78 ± 0.23

Conditions: eluent, 20 mM oxalate–20 mM citrate (pH 3.6) at flow-rate 1.0 ml/min; post-column reagent, 0.2 mM PAR in 1 M ammonium acetate buffer (pH 9.0) at flow-rate 0.7 ml/min and measured at 520 nm.

^a Units for Cu, Co and Ni are $\mu\text{g/g}$ and for Zn, Pb and Fe are % (w/w).

^b ND = Not detectable.

linear in the range 1.0–3.0 $\mu\text{g/ml}$ for Cu²⁺, Ni²⁺, Co²⁺ and Zn²⁺, 8.0–24.0 $\mu\text{g/ml}$ for Pb²⁺ and 2.0–6.0 $\mu\text{g/ml}$ for Fe²⁺. Detection limits for a 24- μl sample solution were 2.2 $\mu\text{g/l}$ for Cu²⁺, 0.9 $\mu\text{g/l}$ for Ni²⁺, 6.6 $\mu\text{g/l}$ for Zn²⁺, 0.9 $\mu\text{g/l}$ for Co²⁺, 1.8 $\mu\text{g/l}$ for Pb²⁺ and 2.1 $\mu\text{g/l}$ for Fe²⁺. Validation of the method by analysing NIST SRM 1648 Urban Particulate Matter and SRM 1633 Coal Fly Ash standard reference materials gave quantitative recoveries (70–100%) for Cu, Zn, Pb and Ni. The results for Pb, Ni and Cu in the total suspended air particulate and respirable particles (PM10) gathered from the Pasir Gudang Industrial Estate, Johor, Malaysia, were

comparable to those obtained by AAS and the results for Fe indicated that part of the iron content in the air particulate samples was probably in the oxidized form.

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Table 4
Comparison of results obtained by graphite furnace AAS and ion chromatography for heavy metals in air particulate samples obtained from the Pasir Gudang Industrial Estate, Malaysia, in September–October 1993

Sample	Metal	n	Concentration ($\mu\text{g}/\text{m}^3$)		F-test ^a
			AAS	IC	
Respirable particles PM10	Pb	12	0.014 \pm 0.001	0.012 \pm 0.003	1.3
	Ni		0.015 \pm 0.002	0.010 \pm 0.007	1.8
	Fe		0.64 \pm 0.07	0.33 \pm 0.12	13.6
	Cu		0.028 \pm 0.005	0.050 \pm 0.022	2.81
Total suspended particles	Pb	8	0.017 \pm 0.004	0.016 \pm 0.006	0.04
	Ni		0.024 \pm 0.005	0.019 \pm 0.009	0.5
	Fe		1.0 \pm 0.1	0.6 \pm 0.1	22.4
	Cu		0.04 \pm 0.01	0.04 \pm 0.02	0.01

^a The critical value for a single-sided F-test with one degree of freedom and 5% significance level is 7.71.

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