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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  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  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 PAR (4-(2-pyridylazo)resorcinol) to form coloured complexes in a postcolumn reactor and detected by using a UV-Vis detector at 520 nm. Detection limits for a 25- $\mu\text{l}$  sample solution were 2.2, 0.9, 6.6 and 1.8  $\mu\text{g/l}$  for respectively metals. The technique was optimized and validated by analysing the NIST standard reference materials SRM 1648 Urban Particulate Matter and SRM 1633b Coal Fly Ash.

### 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 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 chromatographic techniques [3] and by 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 applicability of ion chromatography for the determination of heavy metals ( i.e., Cu, Pb, Zn, and Ni ) 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.

## RESULTS AND DISCUSSIONS

### 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 concentration 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 35mM the retention time was about 40min. An optimum separation of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  was obtained by using an eluent mixture of 20mM oxalic acid and 20mM citric acid at pH 3.6 (Fig. 1A). However, under these conditions  $\text{Fe}^{3+}$  was not separated, probably because it forms a strong  $\text{Fe}(\text{Ox})^{3-}$  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 metals. When the oxalic acid concentration was about 20mM, the optimum concentration of the citric acid was in the range 20-25mM.

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.

### Optimization of detection of metals ions

PAR is generally the most suitable coloured complexant for the detection of heavy metals in UV-Vis spectrophotometry[13]. In this study, the UV-Vis spectra of the PAR

complexes with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  were recorded in ammonium acetate buffer (pH 9.0). The molar absorptivities of these metals at the  $\lambda_{\text{max}}$  and 520nm are given in Table 2. Since the detector was normally set to operate at 520nm, the values of the molar absorptivity at this wavelength indicate the relative sensitivities of the detector towards these metals ions. The data in Table 2 indicate that the relative sensitivities of these metals 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.

**Table 2. Molar absorptivity of the metal-PAR complexes at  $\lambda_{\text{max}}$  and 520 nm recorded in ammonium acetate buffer (pH 9.0)**

Metal-PAR complex	$\lambda_{\text{max}}$ (nm) <sup>a</sup>	Molar absorptivity ( l/mol.cm)	
		$\lambda_{\text{max}}$	520 nm
Pb	520	12210	12210
Zn	495	50110	56701
Cu	500	57123	55778
Ni	490	49177	43709

<sup>a</sup>  $\lambda_{\text{max}}$  is the wavelength at which molar absorptivity is maximum.

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  $\geq 9$  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 the ammonia concentrations were 1.0 and 1.5 M, respectively. At ammonia concentrations below 1.0 M the peak heights of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Zn}^{2+}$  were severely reduced. Reductions in the peak height these metal ions and  $\text{Ni}^{2+}$  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 0.7ml/min (Fig. 1A). When the PCR flow-rate was lowered to 0.4 ml/min, the peak heights of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  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, 20mM oxalic acid-20mM citric acid (pH 3.6, adjusted with LiOH) at a flow-rate of 1.0 ml/min; postcolumn detection with 0.2mM PAR in 1.0mM ammonium acetate buffer at a flow-rate of 0.7ml/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  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  and 8.0-24.0 $\mu\text{g/ml}$  for  $\text{Pb}^{2+}$ . 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 filter 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- $\mu\text{l}$  sample solution the detection limits were 2.2, 0.9, 6.6 and 1.8 $\mu\text{g/l}$  for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ , respectively.

### 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. 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  $\text{Fe}^{2+}$ . With the exception of  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$ , it was apparent that the microwave technique gave satisfactory recoveries (70-100%). Nevertheless, for SRM 1648 Urban Particulate Matter the recovery for  $\text{Co}^{2+}$  was 77%, which was better than those with the hot-plate and the ultrasonication techniques. The recovery of  $\text{Fe}^{2+}$  was consistently low for both samples, which could be due to the predominant oxidized state of the metal ions the samples.

### Analysis of air particulate samples

In addition to the total suspended particulate (i.e., particulate sample collected with the standard high-volume sampler), PM10 respirable particulate samples (i.e., particles with a diameter of less than  $10\mu\text{m}$ , 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 3 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  $\text{Fe}^{2+}$  whereas AAS measures total iron, the significant difference might indicate the nature of the element states in the air particulate samples.

## CONCLUSIONS

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,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  can be separated satisfactorily and detected by UV-Vis spectrophotometry after reaction with PAR. The calibration graphs for these metal ions were linear in the range  $1.0\text{-}3.0\mu\text{g/ml}$  for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ,  $8.0\text{-}24.0\mu\text{g/ml}$  for  $\text{Pb}^{2+}$ . Detection limits for a  $24\text{-}\mu\text{l}$  sample solution were

2.2µg/l for Cu<sup>2+</sup>, 0.9µg for Ni<sup>2+</sup>, 6.6µg/l for Zn<sup>2+</sup> and 1.8µg/l for Pb<sup>2+</sup>. 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.

**Table 3. 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.**

Sample	Metal	Concentration (ug/m <sup>3</sup> )		F-test <sup>a</sup>
		AAS	IC	
Respirable particles PM10	Pb	0.014 ± 0.001	0.012 ± 0.003	1.3
	Ni	0.015 ± 0.002	0.010 ± 0.007	1.8
	Cu	0.028 ± 0.005	0.050 ± 0.022	2.8
Total suspended particles	Pb	0.017 ± 0.004	0.016 ± 0.006	0.04
	Ni	0.024 ± 0.005	0.019 ± 0.009	0.5
	Cu	0.04 ± 0.01	0.04 ± 0.02	0.01

<sup>a</sup> 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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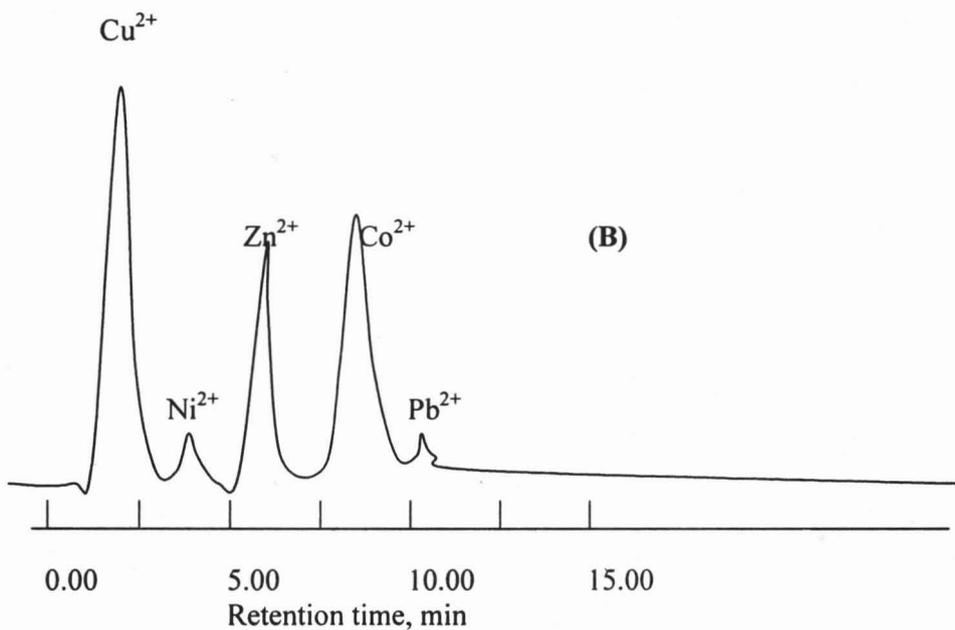
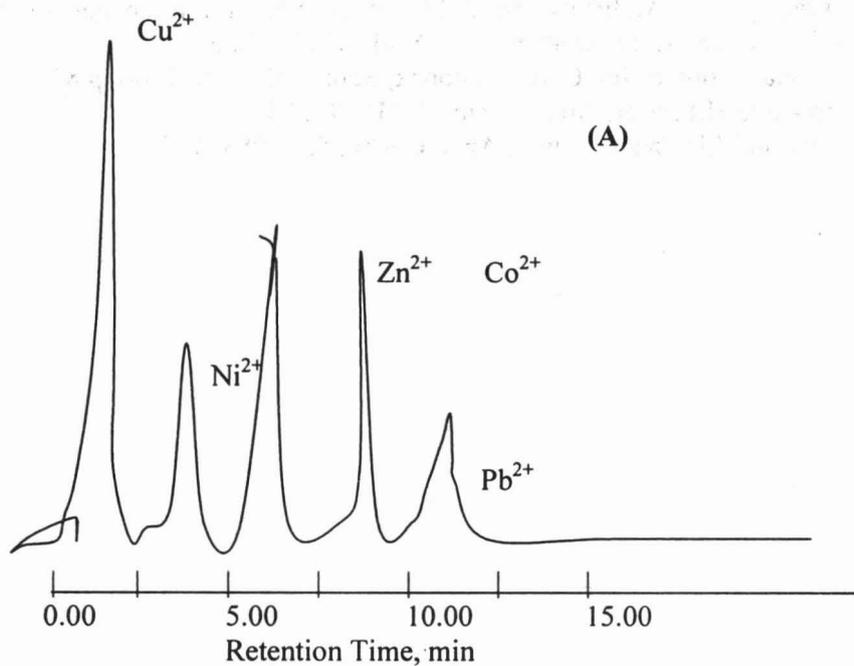


Fig.1. Chromatogram of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  (1.0 ug/ml) and  $\text{Pb}^{2+}$  (8.0 ug/ml) on an IonPac CS2 column. Condition: eluent, 20 mM oxalate-20 mM citrate (pH 3.6) at flow-rate 1.0 ml / min; postcolumn reagent, 0.2 mM PAR in 1 M ammonium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