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Short communication

## Selective ion chromatography of metals on porous graphitic carbon

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### Abstract

The selective retention of trace levels of the transition metal ions,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  on a porous graphitic carbon (PGC) column, is described using ion chromatography with acidified aqueous mobile phases, post-column detection using PAR and spectrophotometric detection. PGC is a selective sorbent for  $\text{Pb}^{2+}$  and for  $\text{Cu}^{2+}$  in aqueous acidified solution, with the latter not eluting from the column. Variation of the concentration of added oxalic acid to the acidified aqueous mobile phase leads to the elution of  $\text{Cu}^{2+}$ , and ion chromatography of a metal mixture of  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  is optimised to give baseline resolution. © 1998 Elsevier Science B.V.

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### 1. Introduction

While the role of carbon-based materials in the solid-phase extraction of organic pollutants, such as volatile organic compounds, has been reviewed [1], the more recent findings on the polar retention effect suggest applications in the trace enrichment and chromatography of polar water soluble solutes. The remarkable ability of porous graphitic carbon (PGC) to retain polar solutes through some kind of electron-transfer mechanism, alongside retention through hydrophobicity has added to the fascination chromatographers are having with this stationary phase. This polar retention effect appears to occur with polar solutes which can either donate or accept electrons, or which can polarise the graphite surface [2].

In particular, the high affinity of PGC for aromatic solutes containing one or more polar substituents has been observed using aqueous mobile phases [3]. The high retention of very polar compounds in water confirms the unique potential of PGC as an ex-

traction sorbent for trace analyses of some water-soluble micropollutants. Knowledge of the retention behaviour of polar pesticides obtained from liquid chromatography on a PGC stationary phase allows the prediction of the conditions for its use as a solid-phase extraction sorbent [4]. Selected polar pesticides and polar degradation products could be quantified at the 0.1  $\mu\text{g}/\text{l}$  level using PGC as a sorbent for their extraction from aqueous samples. By utilising a PGC pre-column and separation column, on-line preconcentration of trace-level pollutants such as 2-chloro-4-aminophenol, chloroanilines, aminophenols and cyanuric acid was achieved [5].

Separation of anionic and cationic compounds of biomedical interest has also been demonstrated on PGC using trifluoroacetic acid (TFA) in the eluent [6]. Highly water-soluble ionizable solutes as oxalic acid, creatine and creatinine can be readily separated from human urine with PGC as stationary phase. It was concluded that the retention of anionic compounds was dominated by electronic interaction between the solute and the delocalized electron

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clouds on graphitized carbon, while cationic species, could be retained by ion suppression or ion pairing consistent with a reversed-phase interaction with the hydrophobic carbon surface.

Modification of the graphite surface with suitable functional groups has generally been deemed necessary for applications in ion analysis. Ion-exchange separations of iodate, nitrite, bromide and nitrate can be achieved on polyethylene imine-coated PGC [7]. In addition in earlier work, as carbon shows irreversible adsorption of selected organic compounds in aqueous conditions, several compounds which have ion-exchange or chelating properties have been adsorbed on granular graphite [8]. Eriochrome Black T modified graphite allows the uptake of  $\text{Fe}^{3+}$  from a multicomponent mixture with  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by controlling the pH. Chelation chromatography using the modified graphite column was shown to be effective for separating specific species such as  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ . In a more recent application of modified graphite in ion-exchange chromatography, a selective metallochromic ligand, *o*-cresolph-talein complexone was used as a dynamic coating for the separation and direct detection of calcium and magnesium in sea-water [9].

Our laboratory has previously developed and characterised linear and macrocyclic chelating silica phases for trace metal preconcentration and ion chromatographic analysis [10,11]. In this paper, the first report of selective retention of trace transition metal ions such as  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  on unmodified PGC is described using ion chromatography (IC) with post-column derivatisation with 4-(2-pyridylazo)resorcinol (PAR) and spectrophotometric detection. The effects of mobile phase pH and added oxalate on metal ion retention are investigated.

## 2. Experimental

### 2.1. Chemicals

All materials, chemicals and solutions were analytical grade. Oxalic acid dihydrate (>99%) and glacial acetic acid (100%) were obtained from Merck (Darmstadt, Germany). Lithium hydroxide and PAR were supplied by Sigma (Poole, UK).

The nitric acid solution was from Wardle Chemi-

icals (Nantwich, UK) and the ammonium hydroxide was from Ashland Chemicals, (Columbus, OH, USA). The divalent metal ion solutions were prepared from 1000 ppm standard solutions of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$  supplied by Merck.

The porous graphitic carbon column, commercially available as Hypercarb (7  $\mu\text{m}$ , 10 cm $\times$ 4.6 mm I.D.) was provided by Hypersil (Runcorn, UK).

### 2.2. Instrumentation

Metal ion separations were carried out on a Dionex 4500I system. This IC system utilised a six-way air solenoid operated microinjection valve and a 25- $\mu\text{l}$  injection loop for sample delivery. The system was equipped with post-column derivatisation with PAR and spectrophotometric detection at 520 nm.

### 2.3. Solution preparation

Deionised water, generated by a Milli-Q deionised water unit which had a resistance better than 18.2 M $\Omega$  cm was used for the preparation of all the solutions.

The metal ions solutions were prepared by dilution of the 1000 ppm standard solutions. The individual concentrations used for injection varied from 1.6 to 40 ppm to aid detectability. A PAR solution of  $5 \cdot 10^{-4}$  M and pH 4.8 was used for post column derivatisation, with detection at 520 nm. This solution was made up in 7.4 M ammonium hydroxide and 1.7 M acetic acid.

Two mobile phase compositions were studied for the elution of the chosen metal ions, namely acidified deionised water, and oxalic acid containing aqueous solutions at selected adjusted pH values. The pH of the mobile phases was adjusted by additions of 1.0–0.05 M LiOH or 1.0–0.05 M  $\text{HNO}_3$ .

### 2.4. Procedures

The mobile phases were degassed in helium for 15 min and the column was equilibrated for 30–45 min with the mobile phase at a flow-rate of 1 ml/min in conjunction with a post-column PAR flow-rate of 0.6

ml/min. Prior to these investigations, the Hypercarb column was put through a washing procedure, involving consecutively passing 0.1 M HCl, water, methanol, 0.1 M NaOH, methanol and finally water for 1 h each at a flow-rate of 1 ml/min.

For each mobile phase, single injections of the seven metals studied were carried out, followed by mixtures of the non-coeluting metals. The retention behaviour of the chosen metal ions was studied by varying two parameters of the mobile phase: the concentration of oxalic acid and the pH.

### 3. Results and discussion

While considered a stronger reversed-phase stationary phase than alkyl-bonded silicas, porous graphitic carbon has, in addition, the ability to retain solutes with polar substituents. This polar retention effect is exemplified by the complete retention of oxalate under aqueous mobile phase conditions. While hydroxyl, carbonyl, carboxylate and *N*-containing groups are expected to be present at edge carbons on the graphite sheets, they are considered to be insignificant in the retention mechanism on a graphite surface, which does not contain ion-exchange sites [2]. Unlike the silanol groups of a silica surface, such functional groups are not in sufficient numbers to represent the anchoring sites for uniform covalent modification of the phase for chromatographic selectivity. To date, this has been achieved by non-covalent modification of the graphite surface through irreversible adsorption of chemical modifiers such as chiral selectors or complexing agents like Eriochrome Black T. However, it appears that modification of PGC is not necessary to obtain metal ion selectivity.

The retention behaviour of the chosen series of metal ions was first investigated by injection of acidic standard solutions onto the column using acidified water as the mobile phase. At pH 1.25, for example, the metal ions were expected to elute at the zero retention time, as would happen on octadecyl silica. Surprisingly,  $\text{Cu}^{2+}$  did not elute at all and  $\text{Pb}^{2+}$  was selectively retained over  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . The chromatogram obtained is shown in Fig. 1. The observed retention is believed to be a further example of an electronic

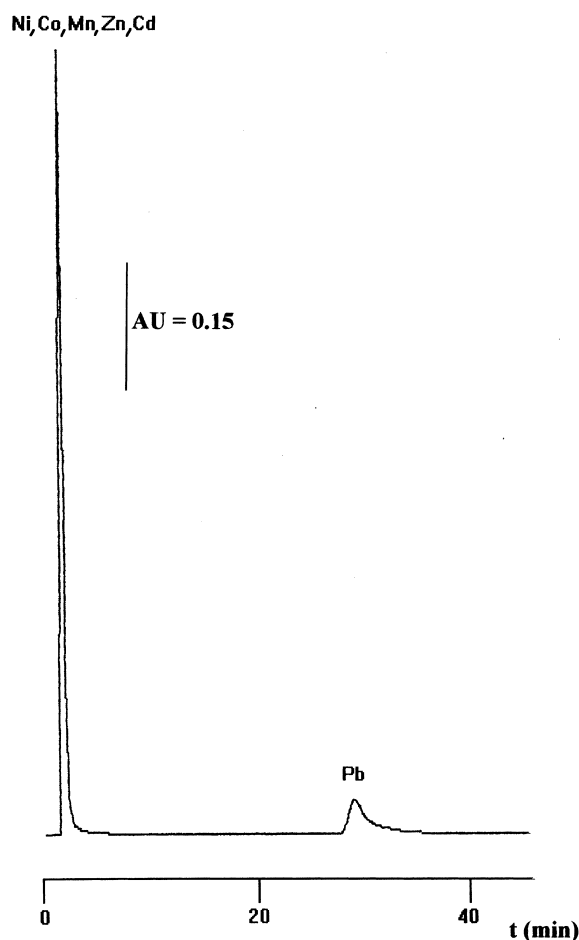


Fig. 1. Chromatogram obtained on injection of metal ion mixture of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  into acidified aqueous mobile phase, pH 1.25. (Note:  $\text{Cu}^{2+}$  is not eluted).

interaction between the graphite and ionic solutes. Such electronic interaction, either by electron donation or acceptance, is presumably between the electronic cloud of the graphite and available orbitals of the metal centres. Furthermore, increasing the pH in increments up to pH 3.5 did result in some increased retention of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . There may be a competition between the proton and metal ions for interaction with the graphite, resulting in increased metal ion retention with increasing pH. Protons may act as an electronic modifier, for elution of the metal ions. Above pH 3, however, the reproducibility of the retention order was poor for  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . PGC in addition, acts as a selective sorbent for  $\text{Cu}^{2+}$

and  $\text{Pb}^{2+}$ , suggesting that a more stable interaction occurs for these metal ions, a feature which could be a result of a preferred planar symmetry which these metal ions can adopt.

Organic ligands, such as oxalate and citrate are widely used to facilitate metal ion separations by cation or anion chromatography [12,13]. Complexation to oxalate can alter the charge on the metal species from cationic to anionic and elution from a cation exchanger is increased with increasing pH, oxalate concentration and metal–oxalate stability constant value. Coincidentally, oxalic acid is known to be totally retained on PGC, unless TFA is added to the eluent as an electronic modifier [6]. Thus the modification of the PGC surface could be expected to occur when the Hypercarb column is equilibrated with an aqueous mobile phase containing oxalic acid. As the native PGC appears to have its own ability to selectively retain cationic metal species, such a modification could be expected to initially at least enhance the retention of metal ions by providing

oxalate complexing sites on the surface. A number of studies of the effect of variation of added oxalic acid to the mobile phase were carried out at acidic pH values. A plot of measured retention times for injected metal ions against oxalic acid molarity, obtained at pH 1.6, is shown in Fig. 2. Taking oxalic acid  $\text{p}K_a$  values as 1.04 and 3.82, the concentration of  $\text{Ox}^{2-}$  can be calculated to increase from  $4.7 \cdot 10^{-6}$  to  $2.1 \cdot 10^{-3} M$  as the added oxalic acid is increased from 0.001 to 0.45  $M$  at pH 1.6. Using tabulated stability constant data for metal ion complexation to the oxalate ligand [14,15], species distribution diagrams constructed as a function of  $\text{p}L$  provide information on the percentage and average ligand number of the complex species formed at this fixed pH. The increase in  $\text{Pb}^{2+}$  retention, as added oxalic acid is increased up to 0.15  $M$ , coincides with the lead species changing from free uncomplexed metal to the neutral 1:1 complex  $\text{PbOx}$  ( $\log \beta_1 = 4.1$ ). Thus  $\text{Pb}^{2+}$  retention appears to be increased by complexation to surface bound oxalate or through the

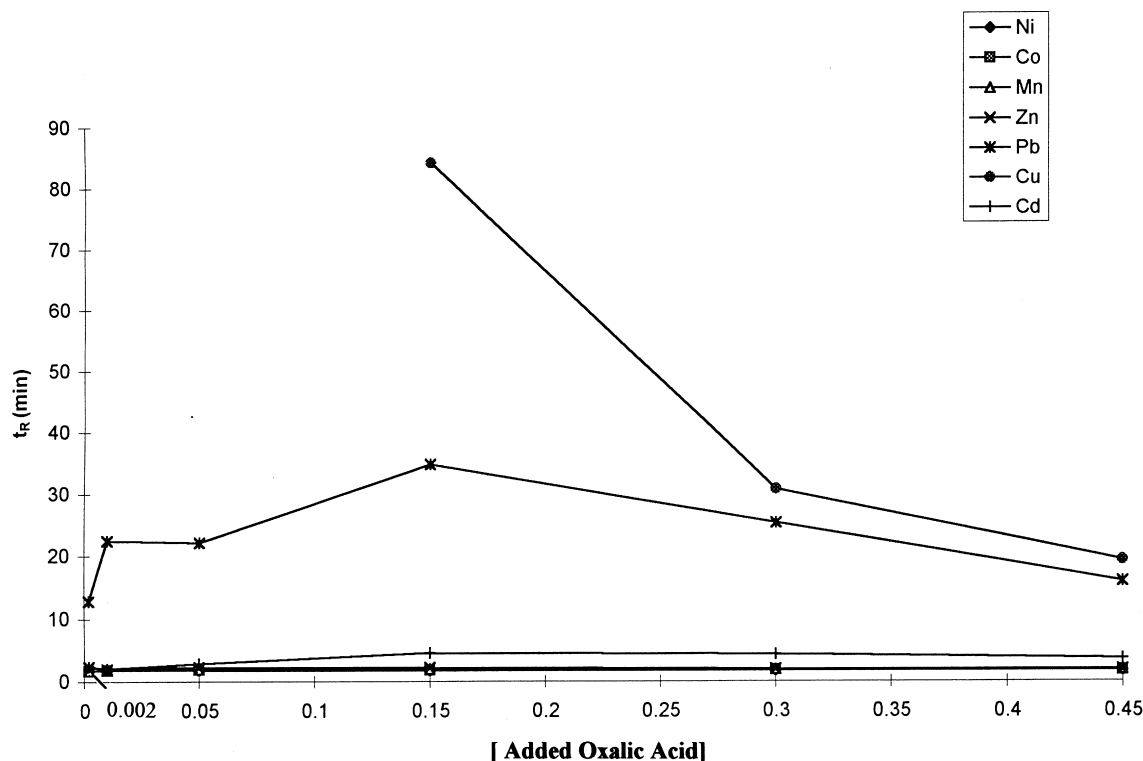


Fig. 2. Plot of measured retention times versus added oxalic acid concentration in the mobile phase at pH 1.6.

hydrophobic partitioning of the neutral complex species. The subsequent reduction in retention of  $\text{Pb}^{2+}$  can be attributed to increasing percentages of the charged  $\text{PbOx}_2^{2-}$  ( $\log \beta_2=6.3$ ) species in the mobile phase. Under the same conditions,  $\text{Cd}^{2+}$  follows the behaviour of lead, but with little inherent affinity for the graphite surface in acidic solution and a lower stability of complexation to oxalate ( $\log \beta_1=2.7$ ), it is eluted at the  $t_0$  as free metal in low oxalate but is somewhat retained when complexed to oxalate at added oxalic acid levels greater than 0.05 M. Baseline resolution of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  from the other injected metal ions is obtained as shown in Fig. 3. At the other extreme,  $\text{Cu}^{2+}$  has the highest affinity for the graphite surface and largest stability constants for oxalate complexation ( $\log \beta_1=6.2$ ;  $\log \beta_2=10.2$ ). It elutes only at high oxalate concentrations, where the  $\text{CuOx}_2^{2-}$  species dominates. Increases in oxalate results in the elution of  $\text{Cu}^{2+}$  from the column and reduced retention times for  $\text{Pb}^{2+}$ , analogous to the role of the oxalate ligand in traditional ion chromatography. A representative chromatogram obtained at pH 1.6 and oxalic acid at 0.45 M for an injected mixture of  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  is

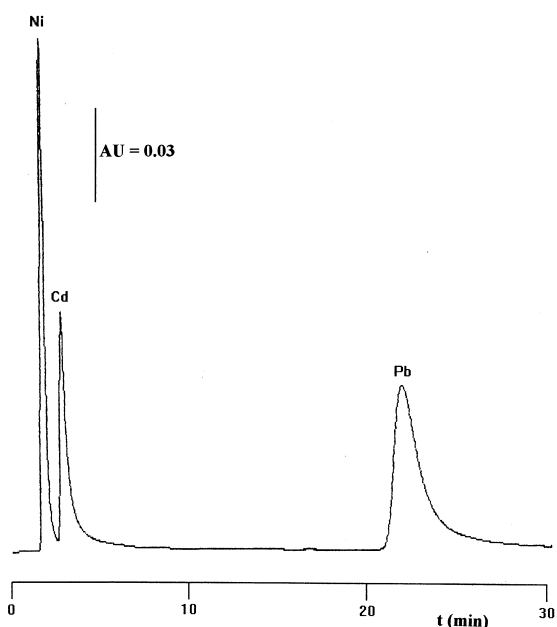


Fig. 3. Typical ion chromatographic separation of Cd and Pb from other metal ions, obtained at low added oxalic acid concentration (0.05 M, pH 1.6).

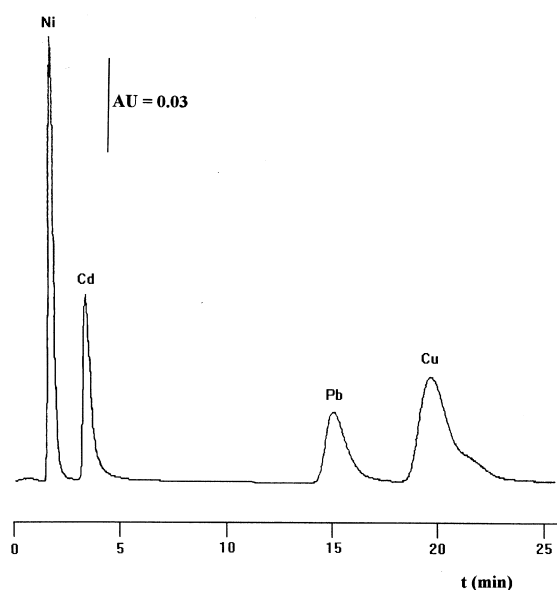


Fig. 4. Ion chromatographic separation of four metal ions,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  on a Hypercarb column at high added oxalic acid concentration (0.45 M, pH 1.6).

shown in Fig. 4, with  $\text{Ni}^{2+}$  essentially unretained. IC of selected metal ions is clearly possible on PGC.

Studies of the variation of pH at constant oxalic acid concentration were also carried out. The effects of increasing pH were most dramatic at low oxalate concentration, such as at 0.01 M as shown in Fig. 5. It is possible to obtain long retention times for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  with  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  completely retained on PGC above pH 3. The increases in retention coincide with increased formation of metal–oxalate complex species, as the competition from protons in the mobile phase is reduced.

#### 4. Conclusions

Using acidified water as the mobile phase, PGC shows complete retention of  $\text{Cu}^{2+}$  and long selective retention of  $\text{Pb}^{2+}$ . The selectivity of native PGC for these metal ions is presumably through electronic interaction between the electronic cloud of the graphite and orbitals of the metal ion centres. Introduction of millimolar oxalic acid into aqueous mobile phases is likely to modify the PGC surface and to increase through complexation the extent and

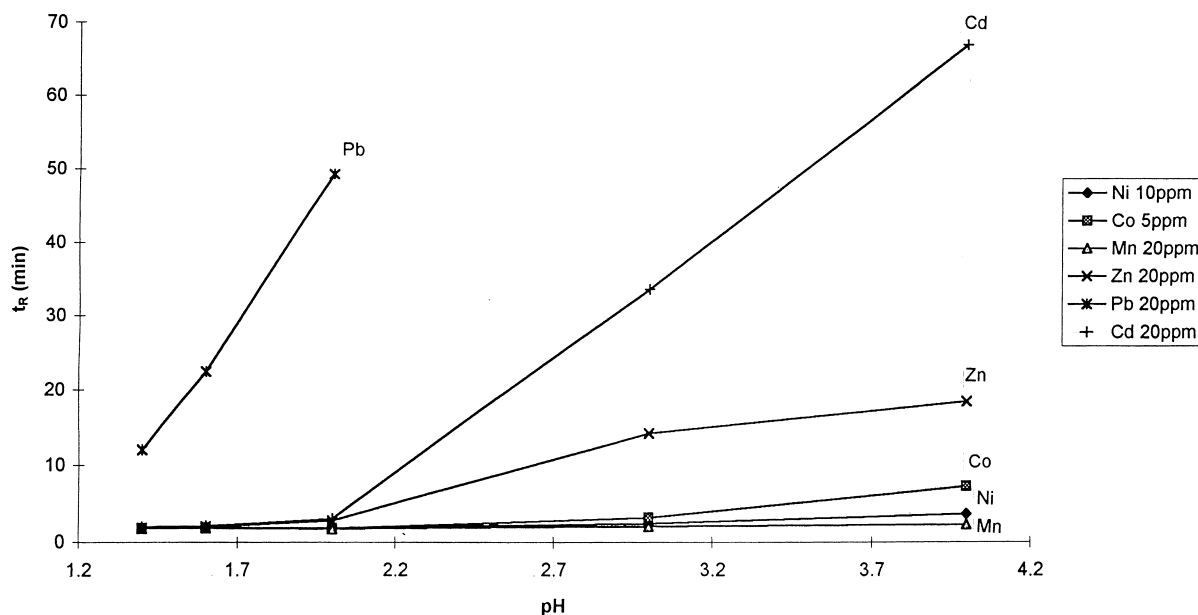


Fig. 5. Dependency of metal ion retention times on mobile phase pH at 0.01 M added oxalic acid.

range of metal ions retained. Increasing pH under these conditions enhances retention such as observed for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . Higher oxalate concentrations act, as expected, predominately as a mobile phase ligand, assisting the elution of the strongly retained  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  metals ions from the PGC stationary phase.

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