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Determination of trace cadmium in environmental water samples using ion-interaction reversed-phase liquid chromatography with fluorescence detection

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Abstract

An ion-interaction reversed-phase liquid chromatographic method has been developed for the determination of cadmium at low μg/l concentrations in environmental water samples. Cadmium and other matrix metals were separated through on-column complexation with 8-hydroxyquinoline sulphonate, using an octadecylsilica column and a mobile phase containing 15% acetonitrile, 10–13 m*M* tetrabutylammonium hydroxide, 5 m*M* 8-hydroxyquinoline 5-sulphonic acid and 10 m*M* acetic acid–acetate buffer (pH 4.8–5.4). Under the above conditions Cd(II) could be easily resolved from excess concentrations of matrix metals and could be detected at concentrations as low as 2 μg/l using fluorescence detection at 500 nm (based upon a 100-μl injection). The method showed a slightly curved detector response over the range of interest [up to 1 mg/l Cd(II)] and was successfully applied to the determination of trace Cd(II) in water samples containing large excesses of Mg(II) and Zn(II) and other matrix metals.

Keywords: Cadmium; 8-Hydroxyquinoline 5-sulphonic acid

1. Introduction

Both 8-hydroxyquinoline (8-HQ) and its more soluble derivative, 8-hydroxyquinoline 5-sulphonic acid (8-HQS), have been used by several workers in differing ways in the liquid chromatography (LC) of metals ions. The reasons for using these ligands include their ability to rapidly form stable complexes with a large range of metals, and the fact that a number of these metal–ligand complexes are fluorescent. These ligands have generally been used in one of three ways, firstly, as post-column reagents, as in the post-column reaction detection system for aluminium species developed by Jones and co-workers [1–3]. Secondly, to form metal complexes ''pre-column'' that are subsequently separated using reversed-phase chromatography, and thirdly as additions to the mobile phase, whereby a combination of ''pre-column'' and ''on-column'' complexation may be utilised. Some of the earliest work in this latter area was carried out by Dasgupta et al. [4]. In this work 8-HQS was added into the mobile phase and used with various types of stationary phases, including reversed-phase, anion and cation exchangers. Some promising separations were obtained using a surface sulphonated cation exchanger. This was particularly the case for Cd(II) and Zn(II), which

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were injected as uncomplexed ions, forming complexes ''on-column'', allowing low μg/l detection limits using fluorescence at 470 nm. However, the peak shapes and resolution obtained using this approach were poor and not suitable for quantitative analysis of real samples. Later Soroka et al. [5], used the same system with gradient elution, achieving the partial separation of Zn(II), Cd(II), Mg(II) and Ca(II) in approximately 8 min.

Work by Meaney and co-workers [6,7] used a reversed-phase system for the separation of Fe(III) and Al(III) complexes of 8-HQ. Metal complexes were formed ''pre-column'' and separated on an octadecylsilica column using an acetonitrile mobile phase containing 10 m*M* 8-HQ and 0.2 *M* KNO_3. The method was applied to various soil digests and water samples. However, the method did result in rather broad peaks, and as the detection method used was UV–Vis at 400 nm, the detection limits were only between 10 and 50 μg/l.

Ion-interaction reversed-phase LC of metal–8-HQS complexes has been carried out by several groups in recent years with varying degrees of success. Shijo et al. [8] successfully separated 8-HQS complexes (again formed pre-column) of Al(III), Cu(II), Ga(III) and Fe(III) by ion-interaction LC, using a mobile phase containing 8-HQS to suppress on-column dissociation and hexylamine hydrochloride as an ion-interaction reagent. However, once again UV–Vis detection was employed which resulted in detection limits of between only 0.05 and 2 mg/l, mainly due to the 8-HQS added to the mobile phase, which caused a significant increase in background absorbance. Similar studies were later carried out by Basova et al. [9] who investigated the use of several ion-interaction reagents, namely tetrabutylammonium, hexadecyltrimethylammonium and heptylamine hydrochloride for the separation of preformed metal–8-HQS complexes, again using UV–Vis detection, although here 8-HQS was not added to the mobile phase to reduce background absorbance.

With fluorescence detection this is much less of a problem, due to 8-HQS not exhibiting fluorescence in its uncomplexed form. Feng et al. [10] recently illustrated this when they studied the retention behaviour of Zn(II)–, Cd(II)–, Al(III)–, Ga(III)– and In(III)–8-HQS complexes on a octadecylsilica column with a mobile phase containing 0.5–4 m*M* 8-HQS, 1–10 m*M* tetrabutylammonium bromide (TBABr) as the ion interaction reagent, and 0.1 *M* of either phosphate or acetate buffer (made up in 20% acetonitrile). Feng et al. focused most of their attention on the retention behaviour of Al(III)–8-HQS complexes, which consistently eluted as two peaks when using a phosphate buffer in the mobile phase. The retention behaviour of Cd(II) and Zn(II) complexes was also investigated. It was stated that the peak for Cd(II) was not observed at a mobile phase pH of below 6 (said to be due to on-column complex dissociation) and that at a pH of above 7 the complex eluted as a strongly skewed peak. Chromatograms of the above metal complexes were not shown, although it is clear that the above mobile phase composition was again not suitable for the quantitative analysis of these metal ions in real samples.

This paper reports on the development of a simple ion-interaction LC method suitable for the determination of trace levels of Cd(II) in environmental water samples. Few simple and sensitive chromatographic methods are available for Cd(II) determinations and the toxic and bio-accumulative nature of this particular heavy metal require such methods be developed. The following method is based upon ''on-column'' formation and separation of metal–8-HQS complexes. The technique resulted in both reduced analysis time (through less sample preparation) and also in improved peak shapes, and therefore lower detection limits, compared to those obtained for complexes formed ''pre-column''. Mobile phase conditions which provided adequate retention and resolution of Cd(II) from other matrix metal ions present in excess, yet still allowing sensitive fluorescence detection, were developed. The method was applied to both a spiked river water sample and a drainage water sample from a disused copper mine.

2. Experimental

2.1. Instrumentation

The LC system used for the initial section of this study consisted of an Varian 9012 Solvent Delivery System (Walnut Creek, CA, USA) and a manual sample injector fitted with either a 100- or a 250-μl

injection loop (Rheodyne, Cotati, CA, USA). A Millipore Waters 470 Scanning Fluorescence Detector (Milford, MA, USA) was used set at an excitation wavelength of 360 nm and an emission wavelength of 500 nm (excitation and emission slits set at 18 nm). The analytical column used was a Millipore Waters Bondapak C_{18} reversed-phase column (300× 3.9 mm I.D.). The flow-rate used was 1.5 ml/min. Later the above pump was replaced with a Dionex Model GPM2 Gradient Pump Module (Sunnyvale, CA, USA). Chromatograms were recorded using Dionex AI450 chromatographic software.

2.2. Reagents

The mobile phase was prepared using deionised water from a Millipore Milli-Q Water Purification System. HPLC-grade acetonitrile (MeCN) was purchased from Lab-Scan (Dublin, Ireland). The ion interaction reagent (IIR), tetrabutylammonium hydroxide (TBAOH), was purchased as a 40% (w/w) solution from Sigma–Aldrich (Dorset, UK), and 8-hydroxyquinoline 5-sulfonic acid hydrate (98%) was also obtained from Sigma–Aldrich. Final mobile phase conditions used were 10 m*M* acetate–acetic acid buffer, 5 m*M* 8-HQS, 10–13 m*M* TBAOH, prepared in acetonitrile–water (15:85) (pH 4.6–5.4). All solutions prepared were filtered through a 0.45-μm filter and degassed using sonication. Low level standard solutions were generally prepared immediately prior to injection, although they remained stable for several days without sign of degradation. Where stated, 8-HQS was added to both standard and sample solutions to obtain a final concentration of 5 m*M* (see Section 3.2).

3. Results and discussion

The aim of this work was to develop a simple, sensitive and selective method for Cd(II) determinations in environmental water samples. Ion-interaction LC was investigated as it required only simple LC instrumentation (no post-column reaction system required) and an inexpensive reversed-phase C_{18} column. As discussed in the Introduction, Feng et al. [10] have shown the possibility of using ion-interaction LC to separate metal–8-HQS complexes followed by their detection using fluorimetry. As Cd(II) forms a strongly fluorescent complex with 8-HQS, this approach was chosen for further development and application to real samples.

In an ion-interaction LC system a number of mobile phase parameters exist which can be changed to control selectivity and analyte resolution. In addition to this, in cases where metal–ligand complexes are being separated, mobile phase conditions can also have an effect upon both peak shapes and detector sensitivity (e.g., the concentration of the ligand in the mobile phase and the mobile phase pH may increase or reduce on-column dissociation). Therefore, in this study it was necessary to understand and develop suitable mobile conditions that provided the desired selectivity, efficiency and sensitivity.

3.1. Development of mobile phase

In this study the concentration of 8-HQS added to the mobile phase was kept constant at 5 m*M*. The reason for this relatively high concentration (compared to previous work [4,5,8–10]) was initially to try to maximise the formation of the ML_2^{2-} complex and limit on-column dissociation to either ML or M^{n+}, as it was first thought this may have lead to poor peak shapes or even completely split peaks. This effect had been shown by Feng et al., for Al(III)–8-HQS complexes. In this case, the second of two peaks obtained for the injected Al(III)–8-HQS standard increased relative to the first when the mobile phase 8-HQS concentration was increased, presumably due to the increased formation of the AlL_3^{3-} complex over the AlL_2^- form. Earlier studies into the chromatographic behaviour of Al(III)–8-HQS complexes [11,12] had shown that such complexes are kinetically inert and so could indeed be separated chromatographically. Cadmium however forms much weaker and more labile complexes with 8-HQS than Al(III), that could not be individually separated under chromatographic conditions. Although, as mentioned previously, due to fast complexation kinetics, the equilibrium is highly labile and so the various Cd(II)–8-HQS complexes should pass through the column as a single sharp band.

In the present study, the above mobile phase conditions produced only single reasonably sharp

peaks for Cd(II) and Zn(II), indicating the assumptions made above to be correct. As sharp peaks were being obtained, the mobile phase concentration of 8-HQS was kept at 5 m*M*.

The concentration of acetate–acetic acid buffer added to the mobile phase was also kept constant at 10 m*M*. The addition of the buffer in this system was carried out not to control analyte retention, (through competition between the acetate and the negatively charged complex for the IIR) but to simply buffer the mobile phase pH. Therefore, the concentration was kept low as this would also limit any unfavourable equilibria, such as those shown once again by Feng et al., who used 0.1 *M* acetate and phosphate buffer concentrations in their mobile phase. Such high concentrations of these anions can not only cause peak splitting but can also drastically reduce sensitivity due to competitive complexation and may even result in the formation of insoluble precipitates within the system, particularly when using phosphate.

The effect of varying the concentration of the IIR in the mobile phase is shown in Fig. 1a [other mobile phase conditions: 10 m*M* buffer (pH 4.6), 5 m*M* 8-HQS, 15% MeCN]. The increase in retention is typical of an ion-interaction retention mechanism and also eludes to the type of metal–ligand complexes being formed/separated. From Fig. 1a it is clear that Al(III) shows a very strong retention compared to the divalent metals. This indicates Al(III) could be being retained as the AlL_3^{3-} species and Cd(II) and Zn(II) may be predominantly forming ML_2^{2-} complexes. For Mg(II), retention does not increase with increasing IIR, indicating Mg(II) passes through the column as either a neutral or slightly cationic species. This is supported by stability constant data which suggests Mg(II) would be only very weakly complexed with 8-HQS at the mobile phase pH used [13]. From Fig. 1a it is clear that the retention of Zn(II) increases more rapidly than that of Cd(II), and that Mg(II) is almost unaffected. Therefore, selectivity for these three metals in real samples can be manipulated through control of this parameter (see Section 3.4).

However, having stated the above regarding the metal–ligand species likely to be being formed, it is clear that in any ion-interaction system the exact retention mechanism involved is difficult to ascertain. It has been assumed by previous workers [8–10] that the metal ions injected first form a negatively charged complex with the 8-HQS (as discussed above) (or are injected as pre-formed complexes), followed by the formation of an ion-pair with the positively charged IIR (which maybe predominantly present in the mobile phase or absorbed onto the stationary phase, or more likely a combination of both). However, in this case it is also possible that the 8-HQS first forms a neutral ion-pair with the IIR and this results in the formation of a dynamic coating on the stationary phase. This would then act as a dynamic chelating stationary phase, with the retention of metal ions being due to stationary phase complexation. In this situation, selectivity would be based upon relative formation constants (K_f) for each metal with 8-HQS, and here as expected retention of the above metal ions increased with increasing K_f [Mg(II) $\beta_1=4.1$, $\beta_2=7.6$, Cd(II) $\beta_1=6.9$, $\beta_2=13.4$, Zn(II) $\beta_1=7.5$, $\beta_2=14.3$, Fe(III) $\beta_1=11.6$, $\beta_2=22.8$] [13] {Al(III) not given in Ref. [13]}. Of course mobile phase complexation must also be occurring,

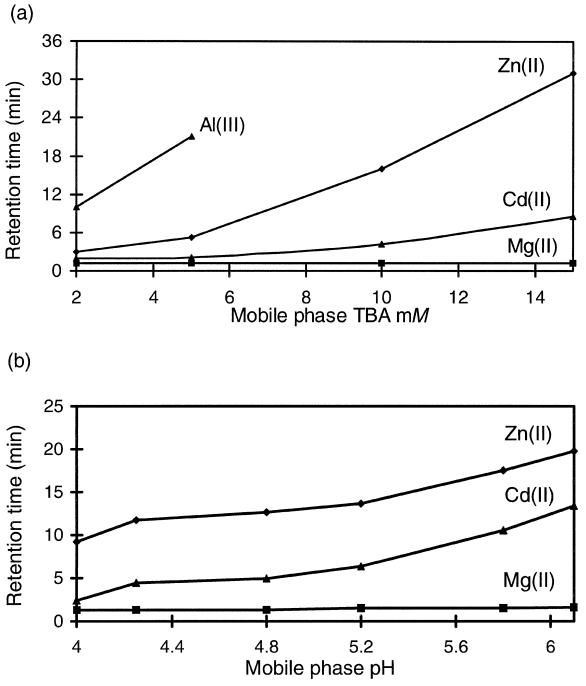

Fig. 1. Effects of mobile phase (a) ion-interaction reagent concentration, (b) pH on retention times for Al(III), Mg(II), Cd(II) and Zn(II). Other conditions see text.

as the metal ions injected would not be detectable if they were not eluting from the column as complexes.

In practice, it is difficult to determine which of the above models is correct for this particular system and the most likely answer is that it may in fact be a combination of both. Increasing the concentration of IIR would result in the observed increase in retention in both cases and so does not help to elucidate the exact mechanism. This is also the case with mobile phase pH (see below).

The effect of mobile phase pH on both retention time and detector sensitivity was investigated over the range 4.0 to 6.1 (other mobile phase conditions: 10 m*M* buffer, 10 m*M* TBA^+, 5 m*M* 8-HQS, 15% MeCN). The pH was not investigated above 6.1 due to solubility problems of both metals and other metals likely to be present in real samples. The results obtained are given in Fig. 1b, showing retention times and in Table 1, showing the effect upon peak areas. As can be seen Cd(II) and Zn(II) again behave very differently to Mg(II), which shows very little response to mobile phase pH, due to the reasons discussed above. Both Cd(II) and Zn(II) show a similar increase in retention over the pH range shown, with little change in resolution of the two metals. The trends shown can again be readily explained with the use of formation constants for each metal–8-HQS complex. Fig. 2 shows the percentage species distribution diagrams for Mg(II), Cd(II) and Zn(II) with 8-HQS over the above pH range. The data is based upon a metal ion concentration of 0.01 m*M* in the presence of 5.0 m*M* 8-HQS and calculated using the formation constants given above (the effect of the presence of 10 m*M* acetate has been ignored). The response for Mg(II) in terms of both retention times and detector sensitivity is clearly (as mentioned above) due to the fact 8-HQS does not begin to complex Mg(II) until pH 5 (ML) and only begins to form the negatively charged species (ML_2^{2-}) at pH 6 and over. This explains why there is a definite rapid increase in detection sensitivity above pH 5 but little or no increase in retention.

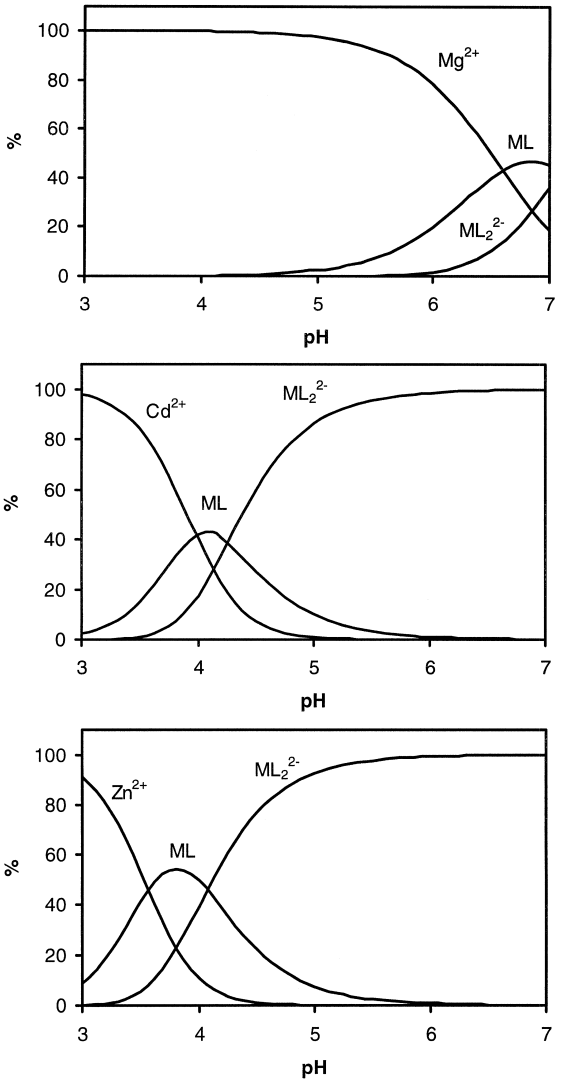

Fig. 2. Percentage species distribution diagrams for Mg(II), Cd(II) and Zn(II) (0.01 m*M*) and 8-HQS (5.0 m*M*).

Table 1
Effect of mobile phase pH on peak area for Mg(II), Cd(II) and Zn(II)

Mobile phase pH	Relative peak area[a]		
	Mg(II)	Cd(II)	Zn(II)
4.0	0.18	0.42	0.64
4.4	0.44	0.77	0.85
4.8	1.00	1.00	1.00
5.1	1.98	1.22	1.16
5.4	3.16	1.41	1.17
5.8	–	1.54	1.23
6.1	–	1.52	1.23

[a] Relative to pH 4.8. Injected standard contained 0.5 mg/l Mg(II), Cd(II) and Zn(II).

For Cd(II) and Zn(II), the retention and detector responses correspond closely to that expected considering the species distribution data shown in Fig. 2. At pH 4 it is only Zn(II) which exhibits significant retention as it is mostly present as either ML or ML_2^{2-}, whereas Cd(II) exists mainly as either M^{2+} or neutral ML. Above pH 4 retention of both metals increases as the percentage of each metal present as ML_2^{2-} increases. Although not investigated for reasons given above, it is reasonable to assume that the increase in retention shown in Fig. 1b would level off above pH 6.1, as at this point practically all the Cd(II) and Zn(II) present should be present as the ML_2^{2-} species. There is also some correlation between the levelling off of the detector response shown in Table 1 for each metal and the pH at which the presence of the free metal (thus non-fluorescent species) becomes insignificant, approximately pH 5.0 for Zn(II) and 5.4 for Cd(II). These results match closely those obtained by Soroka et al. [5], who investigated fluorescence intensity as a function of pH for group II metal–8-HQS complexes.

From the above investigations a mobile phase pH of between 4.8 and 5.4 seemed optimum as this provided reasonable retention times and sensitive detection. Any further increases in peak areas above pH 5.4 did not greatly improve detection limits due to increased peak broadening, making accurate peak integration more difficult.

3.2. "On-column" complexation

As mentioned in the Introduction, 8-HQS has found several uses in chromatographic systems due to its relatively fast complexation kinetics. In this system, the effects of "pre-forming" the metal–ligand complex by adding 8-HQS to the standard and sample solutions, and the effects of simply injecting the metal ions in uncomplexed form were investigated. Fig. 3a and b show two chromatograms obtained from the injection of a 0.5 mg/l standards of Mg(II), Cd(II) and Zn(II). Chromatogram (a) was obtained from the injection of the above metals in water. Chromatogram (b) shows the chromatogram obtained from the injection of standards prepared with the addition of 5 m*M* 8-HQS. It is clear from the two chromatograms that although retention times were unaffected by the form of the injected metal ions, both peak efficiency and consequently peak height, were improved when Cd(II) was injected as the free metal ion. The reason for this is somewhat unclear, although one suggestion would be that, unlike Zn(II), the injected Cd(II) complex had insufficient time to re-equilibrate itself with mobile phase conditions as it passed through the column and so showed clear evidence of peak splitting. However, this clearly seems to contradict the idea that 8-HQS exhibits very favourable complexation kinetics, which must be the case for on-column complexation to be possible in the first place, without resulting in very broad peaks. This splitting effect was not seen with the peak for Zn(II), which eluted as a single well defined peak when injected as either the free ion or complex.

The ability to inject the samples directly without the addition of 8-HQS to the sample is an obvious advantage to this system as it greatly simplified the method and reduced sample preparation and overall analysis time. As the above observations, however contradictory, were very reproducible, for all further work 8-HQS was not added to either standard or sample solutions prior to injection.

3.3. Analytical performance figures

The linearity of the method for Cd(II) was determined using both the standard calibration method and the standard addition technique. Over the range 0–100 μg/l, Cd(II) standards ($n=4$) produced a slightly negatively curved response ($y=0.003x^2+1.57x-1.4$, $R^2=0.997$). A river water sample containing Cd(II) below the method detection limit was spiked with Cd(II) at 25, 50 and 100 μg/l concentrations. The resultant standard addition curve showed a slightly reduced slope to the above standard curve ($y=0.001x^2+1.25x$, $R^2=0.999$), indicating the river water matrix has a slight negative (~20%) effect upon the response for Cd(II), probably due to the presence of unknown complexing or quenching agents [Soroka et al. [5] found Fe(III) to have a drastic quenching effect upon many fluorescent metal–8-HQS complexes and the above river water samples are known to be rich in Fe(III)].

The detection limit for the method was calculated using the signal equal to twice the peak-to-peak

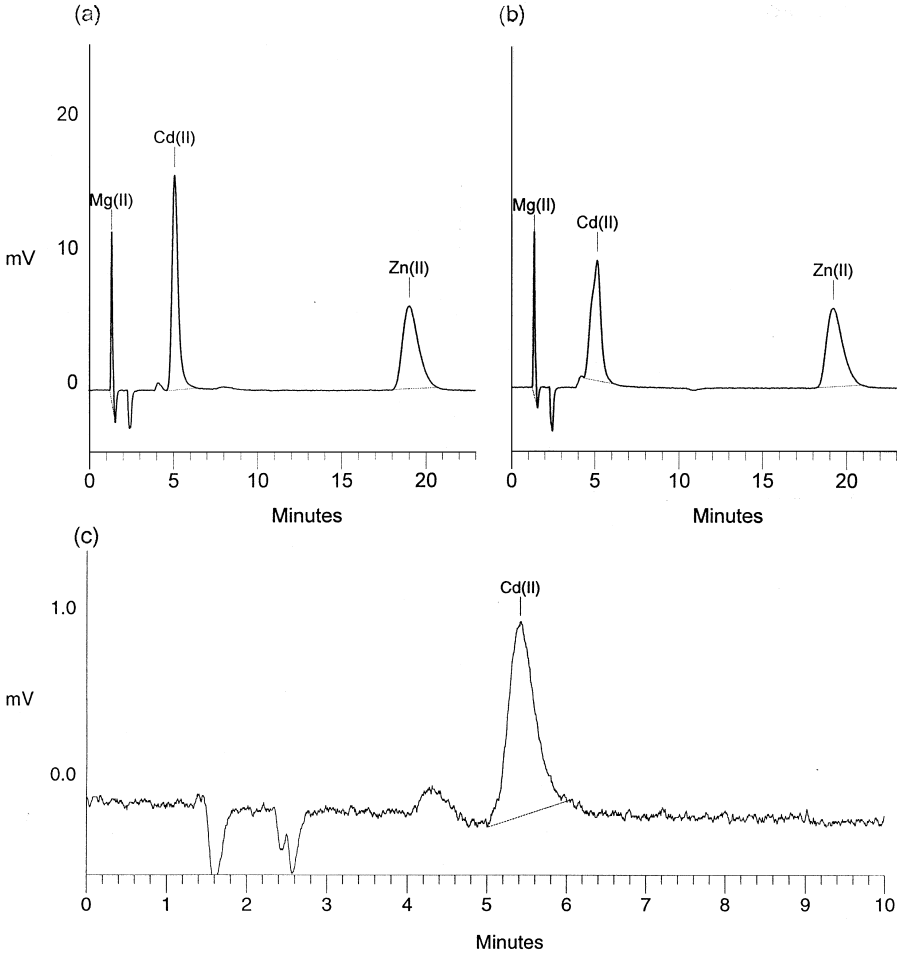

Fig. 3. Chromatograms showing (a) the separation of Mg(II), Cd(II) and Zn(II) (0.5 mg/l) resulting from the injection of the metal ion standards, (b) metal–8-HQS complex standards and (c) the injection of 20 μg/l Cd(II) standard. Other conditions: 10 m*M* buffer (pH 4.8), 12 m*M* TBA^+, 5 m*M* 8-HQS, 15% MeCN.

noise level of the baseline, using mobile phase conditions as in Fig. 3. Based upon a 100-μl injection volume of a standard solution, a detection limit of 2 μg/l was obtained. This was decreased to 1 μg/l through the use of a 250-μl injection loop without significant broadening of the Cd(II) peak. It should be noted that the detection limit achievable using the larger injection loop would be sufficient to detect Cd(II) at concentrations below the US Food and Drug Administration/Environmental Protection Agency (FDA/EPA) maximum permitted levels of 0.01 mg/l for potable drinking waters. Fig. 3c shows the chromatogram obtained from the 100-μl injection of a 20 μg/l Cd(II) standard. The chromatogram shows how the peak for Cd(II) is well resolved from an unknown system peak eluting between 4 and 4.5 min.

Method precision was determined through eight repeat injections of a 100 μg/l standard. Relative standard deviation was determined as 2.2% for retention time, 2.8% for peak height and 3.2% for peak area. The selectivity of the method was investigated through the injection of standards containing 0.5 mg/l of the following metal ions; alkali metals, Ca(II), Ba(II), Sr(II), Mn(II), Pb(II), Co(II), Ni(II), Cu(II), Fe(II), Fe(III) and Al(III). Under the mobile

phase conditions used none of the above standards could be detected. The latter two trivalent metals were fully retained on the column and if necessary, could be removed from the column by using a lower mobile phase pH or IIR concentration or higher MeCN.

3.4. Analysis of water samples

A number of water samples were collected for analysis from a local river system (Avoca River, OS 199825). The river itself flows between two disused mine works where extensive lead, followed by copper extraction was carried out between 1750 to 1982. A sample of the mine drainage water was also collected, which continuously flows into the above river system. The area itself is a popular fishing area and leads to an estuary where shellfish are collected and so the monitoring of heavy metal input due to the mine is of great importance. Fig. 4 shows chromatograms obtained from (a) the injection of a river water sample taken ~100 m downstream of the point of input of the mine drainage flow spiked with 100 μg/l Cd(II) and (b) a similar unspiked sample . It can be seen that the concentration of what could be described as dissolved labile Cd(II) in the river sample is below the detection limit of the method (<2 μg/l). However, it is also clear that between an elution time of 5 and 6 min, there were no interfering peaks arising from the river water matrix.

The chromatogram obtained for the actual mine drainage sample is shown in Fig. 5. The drainage sample had a pH of 2.9 upon collection and was diluted 10-times with deionised water prior to injection due to the high concentration of Mg(II) and Zn(II) in the sample. The concentration of TBA^+ added to the mobile phase was increased to 13 m*M* for the analysis of the river samples to increase the resolution of Cd(II) and Zn(II) and further remove the Cd(II) peak from the system peak which is shown eluting between 4 and 5 min. Analysis of the sample was carried out using standard addition calibration (0–100 μg/l, $n=3$) resulting in a correlation coefficient of $R^2=0.999$. The sample was also analysed using atomic absorption spectroscopy (AAS) for Cd(II), Mg(II) and Zn(II). Table 2 shows concentrations of the above metals present in the undiluted sample. The results show that the concentration of Cd(II) determined using the ion-interaction method matches closely (within 10%) that obtained using AAS. It is also clear from Table 2 and Fig. 5 that Cd(II) can easily be determined at the

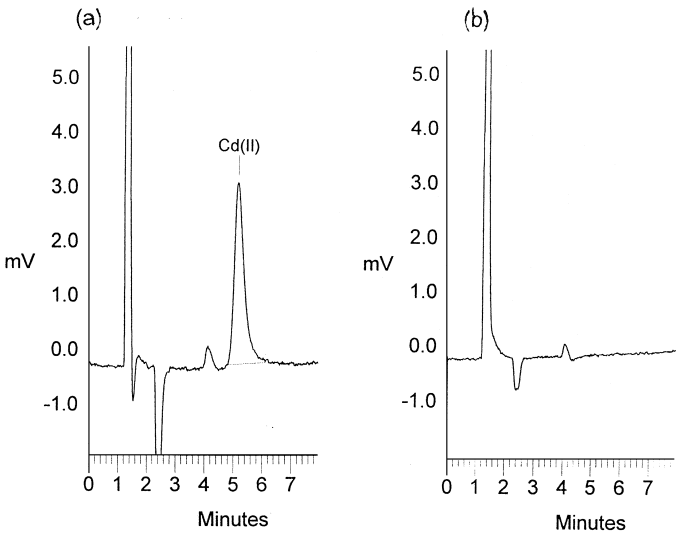

Fig. 4. Chromatograms obtained from (a) an Avoca River sample spiked with 100 μg/l Cd(II) and (b) an Avoca River sample. Other conditions: 10 m*M* buffer (pH 4.8), 13 m*M* TBA^+, 5 m*M* 8-HQS, 15% MeCN.

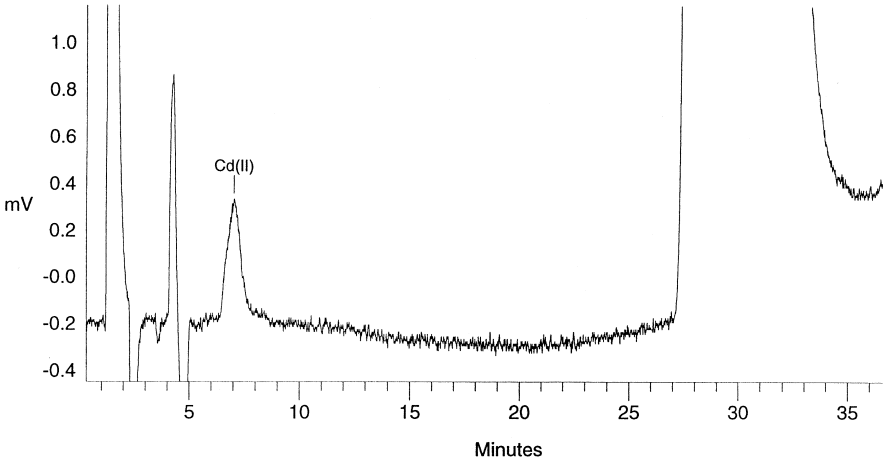

Fig. 5. Chromatogram obtained from the injection of an Avoca Copper Mine drainage sample (diluted ×10). Other conditions as in Fig. 4.

Table 2
Concentration of Cd(II), Zn(II) and Mg(II) in mine drainage sample as determined by ion-interaction LC and atomic absorption spectroscopy

Method	Ion-interaction LC	Atomic absorption spectroscopy		
Metal ion	Cd(II)	Cd(II)	Mg(II)	Zn(II)
Dilution required[a]	×10	×10	×400	×50
Concentration in undiluted mine drainage sample (mg/l)	0.190 (±0.01)	0.174	127	56

[a] Dilution of sample in deionised water prior to analysis. Results based upon triplicate analysis.

low μg/l level in 500–1000-fold excess concentrations of Mg(II) and Zn(II).

4. Conclusions

A simple, sensitive and selective chromatographic method for the determination of Cd(II) in environmental water samples has been developed based on ion-interaction reversed-phase LC combined with fluorescence detection. The method does not require any complicated post-column reactions or time consuming sample preparation. The response for Cd(II) is linear over the concentration range likely to be present in such samples and the method is highly reproducible. In addition, the selectivity of the developed method is such that Cd(II) can be detected at low μg/l concentrations in samples containing excess levels of matrix metals such as alkali and alkaline earths, and those metals which also form fluorescent complexes with 8-HQS, such as Zn(II) and Al(III).

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References

[1] P. Jones, L. Ebdon, T. Williams, Analyst 113 (1988) 641.
[2] P. Jones, Anal. Chim. Acta 258 (1992) 123.
[3] P. Jones, B. Paull, Anal. Proc. 29 (1992) 402.
[4] P.K. Dasgupta, K. Soroka, R.S. Vithanage, J. Liq. Chromatogr. 10 (1987) 3287.
[5] K. Soroka, R.S. Vithanage, D.A. Phillips, B. Walker, P.K. Dasgupta, Anal. Chem. 59 (1987) 629.

[6] M. Meaney, M. Connor, C. Breen, M.R. Symth, J. Chromatogr. 449 (1988) 241.
[7] E. Ryan, M. Meaney, Analyst 117 (1992) 1435.
[8] Y. Shijo, A. Saitoh, K. Suzuki, Chem. Lett. (1989) 181.
[9] E.M. Basova, L.M. Demurov, O.A. Shpigun, J. Van Iyuchun, Anal. Chem. 49 (1994) 735.
[10] Y.Q. Feng, M. Shibukawa, K. Oguma, Chromatographia 41 (1995) 532.
[11] P.M. Bertsch, M.A. Anderson, Anal. Chem. 61 (1989) 535.
[12] S. Motellier, H. Pitsch, J. Chromatogr. A 660 (1994) 211.
[13] A.E. Martell, R.M. Smith, in: Critical Stability Constants, Vol. 5, Plenum Press, New York, 1982, p. 245, Supplement No. 1.