Application of thermal lens spectrometric detection to the determination of heavy metals by ion chromatography

Mateja Šikovec[a], Milko Novič[b], Mladen Franko[a,c,*]

[a]Jožef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia
[b]National Institute of Chemistry, Ljubljana, Slovenia
[c]School of Environmental Sciences, P.O. Box 301, 5001 Nova Gorica, Slovenia

Abstract

Dual-beam thermal lens spectrometry (TLS) was tested as a potential detection technique after the ion chromatographic separation of some heavy metals. Before detection, heavy metal ions of interest (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+} and Fe^{3+}) were separated on a Dionex HPIC-CS5 separation column. For the separation of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}, oxalic acid was added to form anionic and cationic metal complexes, which were then separated on the same column. For the separation of Fe^{2+} and Fe^{3+}, pyridine-2,6-dicarboxylic acid was added to the eluent and iron species were separated as anions. 4-(2-Pyridylazo)resorcinol was used as a postcolumn reagent to form absorbing metal complexes characterized by an absorption maximum at 520 nm. For Cu^{2+} and Co^{2+} ions, TLS detection at 514.5 nm was found to be advantageous compared with UV–Vis detection at 520 nm ($\lambda_{max.} = 520$ nm), whereas for Zn^{2+} and Ni^{2+} the detection limits of the two techniques were comparable.

Keywords: Detection, LC; Thermal lens spectrometry; Derivatization, LC; Heavy metals; Metal ions; Pyridylazo resorcinol

1. Introduction

Since its introduction in 1975 [1] and particularly during the past decade, ion chromatography (IC) has become a well established method for the determination of heavy metals in a variety of samples [2–4]. IC offers several advantages over classical methods used for the determination of heavy metals, including its simplicity of operation and the possibility of a relatively inexpensive upgrade of the IC system when used for other ion analyses, the capability

for speciation analysis [2–8] and the possibility of on-line matrix elimination and sample preconcentration on an appropriate column [9–13], which results in low limits of detection.

In addition to the lowering of the detection limit by introducing a preconcentration column, extensive work has been carried out to improve the detection limits of IC by introducing new detection principles. Because of the relatively complex composition of the eluent, direct conductivity detection is seldom applied [14], and suppressed conductivity detection is impossible owing to on-suppressor formation of insoluble hydroxides. More frequently, element-specific

* Corresponding author.

detection techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace AAS (GF-AAS) and ICP mass spectrometry (ICP-MS) have been applied in IC. These techniques offer excellent detection limits and reproducibility, but their general applicability in routine analysis is limited, mostly owing to the relatively high cost of the equipment, and also complexity of operation (ICP-MS) and inconvenience for on-line detection (GF-AAS).

Owing to these disadvantages of sophisticated element-specific detection methods (particularly GF-AAS, ICP-AES and ICP-MS), UV–Vis spectrophotometric detection is widely used in IC. In the case of heavy metal ions, this method is based on the measurement of the absorbance of coloured complexes obtained when a chromogenic reagent is added postcolumn to the eluent. Different chromogenic reagents, e.g., Arzenazo III, Tiron and 4-(2-pyridylazo)resorcinol (PAR), have been tested for this purpose, it has been found that PAR is the most appropriate reagent owing to its high molar absorptivity (>20 000) between 500 and 540 nm [15,16]. By combining preconcentration and spectrophotometric detection, very low detection limits (ppb range) for individual heavy metals have been reported [9–13]. In general, however, the application of UV–Vis detection is frequently hindered by the relatively low sensitivity and high limits of detection (LODs) compared with some element-specific spectroscopic techniques.

To improve the detection limits, other more sensitive but still relatively inexpensive and easy to operate detection systems should be applied. It has been reported recently [6] that the detection of Cr^{6+} and Cr^{3+} based on the thermal lens spectrometry (TLS), which is well known for its high sensitivity [17], can be used in IC to provide better LODs than classical spectrophotometric detection, and comparable to those obtained by ICP-MS [18].

It was the objective of this work to evaluate the applicability and limitations of TLS detection in IC separations of different heavy metal ions and to investigate the influence of experimental parameters such as excitation laser power on the

TLS signal. Since TLS is a background-limited technique, it was of particular interest to investigate the effect of postcolumn reagent concentration (background absorbance) on the LOD and the overall performance of the analytical procedure.

2. Experimental

2.1. Reagents

All reagents used were of trace metal grade and all solutions were prepared using 18 MΩ/cm deionized water. Stock standard solutions containing 1 mg/ml of metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+} and Fe^{3+}) were prepared and acidified with HCl to pH 1. Working standard solutions were obtained by appropriately diluting the stock standard solutions with 0.1 M HCl.

2.2. Chromatographic conditions

The metal-free chromatographic system consisted of a Spectra System HPLC pump (Model P 4000), a Rheodyne injection valve with a 200-μl sample loop, a Dionex HPIC-CG5 guard column (50 mm × 4 mm I.D.) and a Dionex HPIC-CS5 separation column (250 mm × 4 mm I.D.) attached to the on-line membrane postcolumn reactor, and further to the flow-through cell (Helma, volume 15 μl, path length 1 cm). The PAR reagent was delivered to the system at 0.7 ml/min by using a Dionex pneumatic postcolumn reagent-delivery module.

The eluent used in the mixed separation mode was 50 mM oxalic acid–95 mM lithium hydroxide and that in the anion-exchange separation mode was 6 mM pyridine-2,6-dicarboxylic acid–50 mM acetic acid–50 mM sodium acetate. For both separation modes the eluent flow-rate was 1 ml/min.

The postcolumn reagent stock solution containing 0.2 mM PAR, 1 M acetic acid and 3 M ammonia solution was further diluted to 33%, 20% or 5% by adding appropriate amounts of 1 M acetic acid–3 M ammonia solution.

2.3. Thermal lens detector

A conventional dual-beam thermal lens detector was used. A detailed description of the instrumental set-up, which uses an argon ion laser (Spectra-Physics, Model 2025-25) as an excitation source (514.5 nm wavelength) and a helium–neon laser (Uniphase, Model 1103P) as a probe (632.8 nm wavelength) has been given elsewhere [6].

3. Results and discussion

The signal in a thermal lens experiment is most frequently described as a relative change in the probe beam intensity ($\Delta I/I$), which depends on the sample absorbance (A), the temperature coefficient of its refractive index (dn/dT), thermal conductivity (k), probe beam wavelength (λ) and pump laser power (P):

$$\frac{\Delta I}{I} = \frac{1.21 \cdot A(-dn/dT)P}{\lambda k}$$

The signal and the sensitivity of the technique can therefore be increased by simply increasing the laser power. The thermal lens technique is, however, a background-limited technique and increasing the laser power does not always mean an increase in the signal-to-noise ratio, which is associated with lowering of the LOD. The background signal (the blank) is a particular problem when reagents that absorb considerably in the wavelength range of the pump laser are used. Such was the case in this work, where the background absorbance of the postcolumn reagent (PAR) and its complexes with metal impurities in the eluent resulted in high thermal lens signals.

Reduction of the background signal was therefore attempted by reducing the concentration of the postcolumn reagent. A clear decrease in the background signal (baseline) was observed when the postcolumn reagent was diluted by fivefold, as shown in Fig. 1. This was also accompanied by a decrease in the baseline noise. However, certain peaks in the chromatogram decreased when the concentration of the postcolumn reagent was

reduced. The most significant decreases were observed for the Pb^{2+} and Zn^{2+} peaks, whereas the Cu^{2+} and Co^{2-} peaks were not affected. This indicated that some metal ions form less stable complexes with PAR, and therefore the postcolumn reagent concentration should be optimized for each element separately and also for simultaneous multi-element analysis. At the same time, the laser power had to be optimized to obtain the best LOD.

As demonstrated in Fig. 2, a two-fold increase in the Cu^{2+} peak height was obtained when the laser power was raised from 50 to 95 mW. No increase in baseline noise was observed despite the significantly higher baseline level. At laser powers higher than 95 mW the baseline noise, however, started to increase, and therefore laser powers of 95 mW or lower were always used in this work.

Table 1 summarizes the results of postcolumn reagent concentration optimization and compares the LODs obtained by TLS and UV–Vis detection. It is interesting that despite the significant reduction in the Pb^{2+}, Zn^{2+} and Ni^{2+} peaks, an improvement in the LODs of these elements is obtained on fivefold dilution of the postcolumn reagent. This is because the decrease in the background signal from PAR and the associated decrease in the baseline noise are almost fourfold, whereas the decreases in peak heights of Pb^{2+}, Zn^{2+} and Ni^{2-} are only about 2–2.5-fold. An improvement in the LODs by further dilution of the postcolumn reagent is possible only in the case of Cu^{2+} and Co^{2+}, however, which form more stable complexes and therefore are not affected by dilution of PAR. The observed improvement in the LOD compared with UV–Vis detection (Fig. 3) is over threefold for Cu^{2+} and almost fourfold for Co^{2+}. The LODs for the other metal ions at only 5% of original postcolumn reagent concentration are however, much higher compared with 20% PAR, which was found to be the most suitable for the simultaneous measurement of all investigated ions. Under these conditions the LODs for Cu^{2+} and Co^{2+} are still better than with UV–Vis detection, whereas the LODs for the other ions are comparable except for Cd^{2+}, which obviously
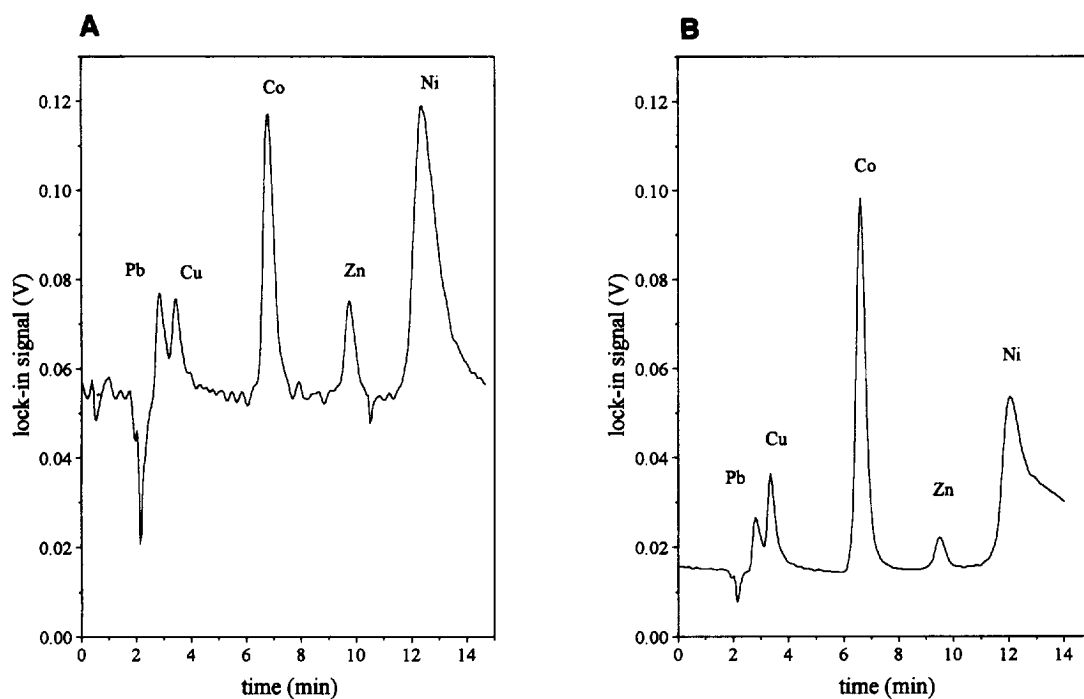
Fig. 1. Chromatograms of samples containing 6 mg/l Pb^{2+}, 0.5 mg/l Cu^{2+}, 2 mg/l Co^{2+}, 2 mg/l Zn^{2+} and 5 mg/l Ni^{2+}. Excitation power, 20 mW. (A) 100% postcolumn reagent; (B) 20% postcolumn reagent.
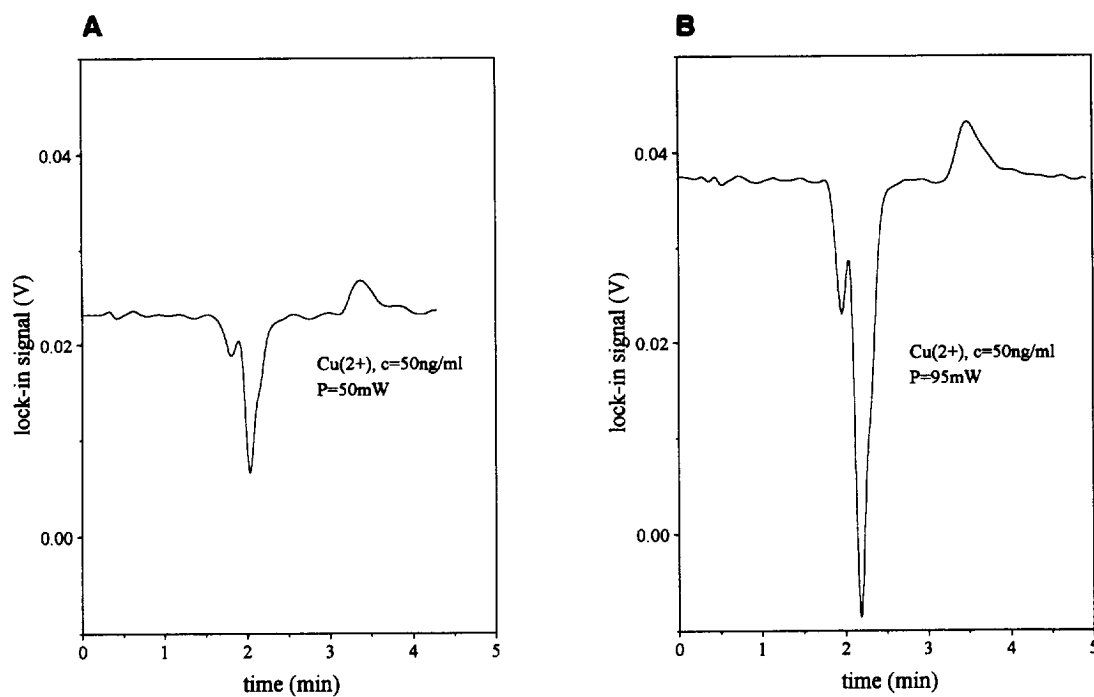

Fig. 2. Effect of pump laser power on peak heights and baseline noise. 5% postcolumn reagent. (A) P = 50 mW; (B) P = 95 mW.

Table 1
Comparison of limits of detection ($\mu g/ml$) with TLS and UV–Vis detection for metal ion–PAR complexes after separation by using the Dionex HPIC-CS5 column

Ion	TLS				
	UV–Vis (100% PAR)	100% PAR	33% PAR	20% PAR	5% PAR
Pb^{2+}	–	0.390	0.324	0.144	–
Cu^{2+}	0.017	0.035	0.020	0.007	0.005
Cd^{2+}	0.110	–	–	0.840	4.0
Co^{2+}	0.015	0.047	0.023	0.007	0.004
Zn^{2+}	0.025	0.140	0.130	0.090	0.30
Ni^{2+}	0.040	0.110	0.075	0.040	0.10

forms the least stable complex with PAR among all the metal ions investigated.

The detection of Fe^{2+} and its separation from Fe^{3+} was attempted. As shown in Fig. 4, when only Fe^{2+} was injected it could not be detected at concentrations below 100 ng/ml, owing to its oxidation by the oxygen present in the eluent and in the chromatographic columns. This could be avoided by pumping 0.1 M sodium sulfite solution through the columns for 2 h, as suggested by the column manufacturer [5]. As indicated by the presence of Fe^{3+} in both chromatograms, partial oxidation of Fe^{2+} also occurs when larger amounts of Fe^{2+} are injected. Neverthe-
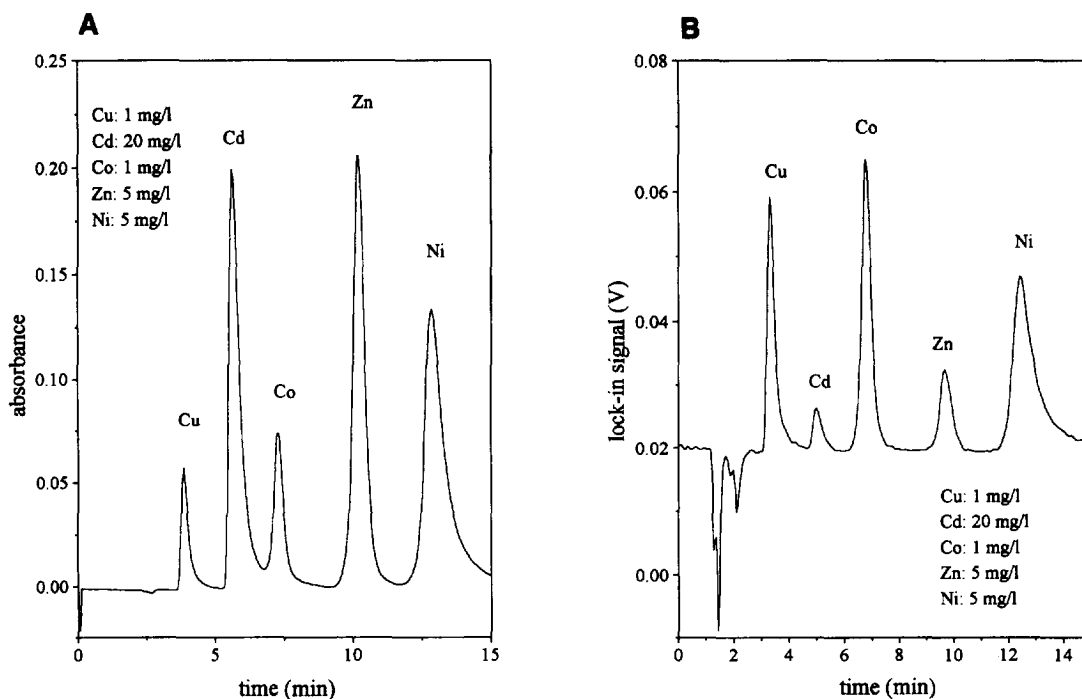

Fig. 3. Chromatograms of samples containing various metal ions. (A) UV–Vis detection, 100% postcolumn reagent; (B) $P = 20$ mW, 20% post column reagent.
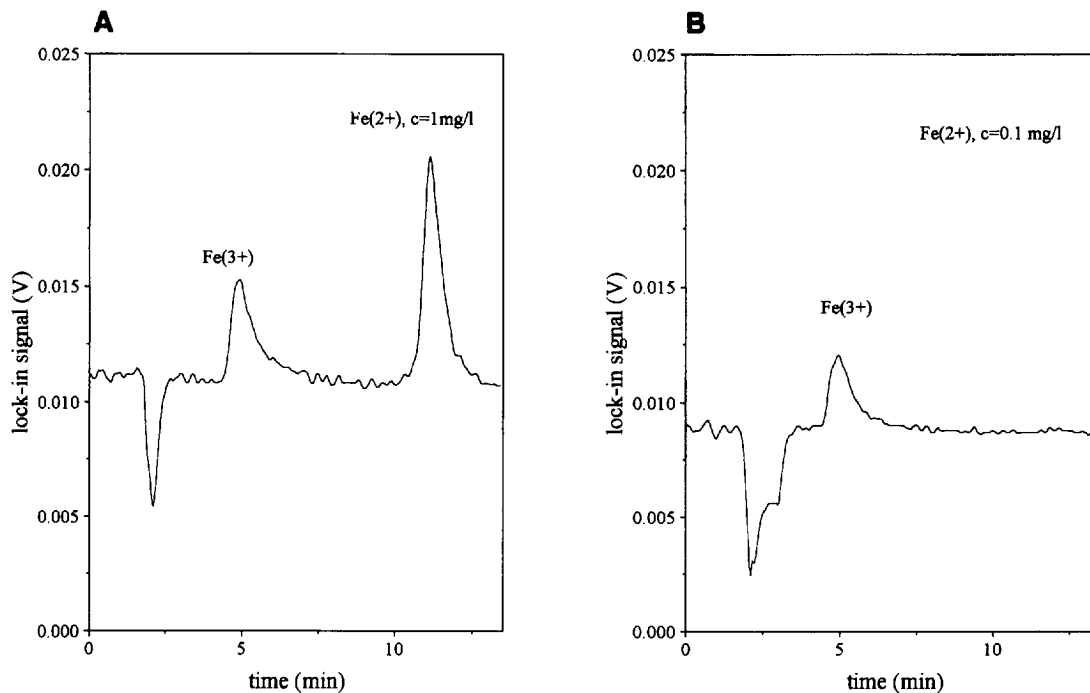
Fig. 4. Effects of on-column oxidation on chromatograms of samples containing different concentrations of Fe^{2+}. $P = 95$ mW; 5% postcolumn reagent.

less, the peaks from each iron species are well separated under selected chromatographic conditions, and Fe^{3+} can be detected at concentrations well below 100 ng/ml (LOD = 20 ng/ml). About the same LOD should also be obtained for Fe^{2+} if the chromatographic conditions are optimized in order to eliminate its oxidation.

4. Conclusions

The relatively high background absorption resulting from PAR severely hinders the LOD in the case of TLS detection by increasing the level of noise relative to the signals from the metal complexes. Decreasing the PAR concentration, in principle, results in a reduction of the background noise and an improvement in the LOD. However, such improvements were observed only for Cu^{2+} and Co^{2+}. A decrease in peak

heights with decreasing PAR concentration was observed for the other ions investigated (Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+}) and can be attributed to the lower stability of their complexes with PAR. As a result, in the case of Cu^{2+} and Co^{2+} TLS detection at 514.5 nm is advantageous compared with UV–Vis detection at 520 nm ($\lambda_{max.} = 520$ nm). In the case of Zn^{2+} and Ni^{2+} the LODs of the two techniques are comparable. A detection limit of 20 ng/ml was obtained for the determination of Fe^{3+} and should be approximately the same for Fe^{2+}. However, the oxidation of Fe^{2+} could not be completely eliminated. Therefore, Fe^{2+} at concentrations below 100 ng/ml could not be detected.

It has been demonstrated that TLS is a simple and sensitive technique for the on-line detection of several metal ions after IC separation. Further improvements in sensitivity and LOD should be possible by using colourless and/or specific postcolumn reagents, e.g., 1,10-phenanthroline in the

case of iron ions. Investigations of background signal reduction by employing the differential thermal lens configuration are in progress.

Acknowledgement

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