POSTER

Stefan Wilke · Hanming Wang
Malgorzata Muraczewska · Helmut Müller

Amperometric detection of heavy metal ions in ion pair chromatography at an array of water/nitrobenzene micro interfaces

Abstract A novel amperometric detector for heavy metal ions has been developed and successfully applied for ion pair chromatography. The detector is based on the electrochemical transfer of the metal ions across an array of water/nitrobenzene micro interfaces. The ion transfer is facilitated by the neutral ionophores methylenebis(diphenylphosphineoxide) and methylenebis(diphenylphosphinesulfide). More than eight metals are separated in less than 15 min on an RP18 column using octyl sulfonate as ion pair reagent. For the heavy metals, the limits of decision are 19(Pb^{2+}), 9(Zn^{2+}), 9l (Co^{2+}), 8(Cd^{2+}) and 1.6(Mn^{2+}) µg/L. The applicability of the new method for water samples is demonstrated.

Introduction

Electrochemical studies on the ion transfer across charged liquid/liquid (L/L) interfaces carried out over the last 20 years have shown that these interfaces can be employed for the voltammetric and amperometric determination of ions as an alternative to the common potentiometric method (for reviews, see [1–3]). Voltammetric and amperometric methods have the advantage that the electrical current signal is directly proportional to the concentration, and that the selectivity of the detector can be varied by means of the electrode potential. The simultaneous determination of Na^+ and K^+ in mineral water [4], the cyclic voltammetric determination of iodide and quinine in

pharmaceutical products [5], and the determination of nitrate and chloride in river water employing the flow-injection technique [6] are examples for the successful application of these new electrode systems for measurements of ions. Neutral species, e.g. volatile amines in fish [7] and the antibiotics terramycin [8], monensin and lasalocid [9] have also been determined in real samples. Sensors for urea and creatinine based on ion transfer across L/L interfaces were described recently [10, 11].

As for potentiometry with ion-selective electrodes, the selectivity of amperometrically working electrodes is limited by the standard Gibbs energy of partition and therefore not always satisfactory for analytical applications. For a number of cations, the selectivity can be enhanced considerably by highly selective ionophores.

A basically different and for many applications more promising approach is, to employ the ion transfer as a non-specific detector in high performance liquid chromatography (HPLC) [12] or capillary electrophoresis (CE). Heavy metal ions can be separated, for example, by ion exchange and ion pair chromatography [13, 14]. Usually, the metals are detected by spectrophotometry after a photometric reagent has been added to the effluent [14]. A disadvantage of this technique is, that it causes an additional peak broadening that could affect the performance of the separation.

The aim of this paper is to present an amperometric detector for heavy metals based on the transfer across an array of L/L micro interfaces [15], and to demonstrate its applicability for the detection of these metals in a chromatographic system. In previous experiments, a mixture of the two bidentate ligands methylenebis(diphenylphosphineoxide) (MBDPO) [16, 17] and methylenebis(diphenylphosphinesulfide) (MBDPS) as co-ligand was found to be suitable as ionophore for this purpose. The detector is based on the transfer of the metal ion M^{z+} from the aqueous effluent (w) into the organic phase (o) facilitated by the neutral ionophore

S. Wilke (✉) · Hanming Wang[1] · M. Muraczewska[2] · H. Müller
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Chemie, D-06217 Merseburg, Germany

[1] On leave from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences

[2] *Present address*: Institut für Chemo- und Biosensorik, Münster, Germany

L in the organic phase:

$$M^{z+}(w) + nL(o) \rightleftarrows ML_n^{z+}(o)$$
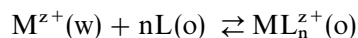
Experimental

The HPLC system comprised a HPLC pump (model 64, Knauer), an injection valve (100 μL, Knauer), the separation column (Eurosphere 100-C18, 5 μm, 120 mm × 4 mm, Knauer) with an integrated pre-column (5 mm × 4 mm), and the electrochemical detector. The flow rate of the eluent was 1 mL/min. The column was allowed to equilibrate with the flowing eluent for 30 min.

The design of the electrochemical flow-through cell and the purification of nitrobenzene were the same as already described in Ref. [6]. In comparison with the previous cell, the membrane was replaced by an array of 110 microholes in a film from polyester (Mylar, 12 μm thickness). The holes were drilled in a hexagonal pattern using a laser ablation technique [18, 19]. The radius of the holes was 8 μm, while the distance between them was 80 μm (center to center). The inner compartment of the cell was filled with 150 μL nitrobenzene, containing 10 mmol/L of the supporting electrolyte PNPDCC [20] and 10 mmol/L of the ionophores MBDPO and MBDPS in each case. A silver wire in the organic phase and a Ag/AgCl electrode (saturated with KCl) served as reference electrodes. The four-electrode potentiostat used was already described previously [21]. No compensation of the IR drop was applied. The current signal was filtered using a low-pass filter of second order (1 s, Bessel). An 18-bits A/D interface MAX132evkit (Maxim) was used to measure the data and to send them to a PC compatible computer. MBDPO and MBDPS were synthesised as described in Ref. [22]. All other reagents were from analytical grade and used as received. The aqueous solutions were prepared from deionised water of 18 MΩ×cm (ELGASTAT UHQ PS, ELGA Ltd.). Measurements were carried out at laboratory temperature (25 ± 2 °C).

Results and discussion

First investigations with the electrochemical detector have shown, that the particular requirements of the electrochemical detector must be considered for the choice of the chromatographic conditions. Usually, strongly complexing eluents based on oxalic, tartaric, citric or dipicolinic acid are employed to separate the metals on a cation exchange column [23] or a special column with both cation and anion exchange properties [13]. The strong complexation of the metal ions in the aqueous effluent phase is the reason, that a higher potential difference between the aqueous and the organic phase is needed to transfer the metal cations into the organic phase. This means, that the voltammetric half-wave potential is shifted towards more positive values. Since the applicable working potential is limited by the transfer of the supporting electrolyte, no (or only very small) signals are observed when the complexes in the aqueous phase are too stable. The use of stronger ionophores, which form more stable complexes with the metal ions in the organic phase, should solve this problem. Since no stronger ionophores were available so far, the only approach to achieve compatibility between separation and detection was to use a column of a smaller ion-exchange capacity. Weak eluents can be

used for the elution of the metals then. The ion pair chromatography (IPC) was employed to realise a column of the desired low capacity [14]. The capacity can be easily adjusted by varying the concentration of the ion pair reagent octylsulfonate (OS) in the eluent [14]. The retention times were found to be proportional to the concentration of OS in the range 0.1–1 mmol/L. The maximum composition of the eluent, with respect to both separation and detection, was found to be 9 mmol/L tartaric acid, 0.7 mmol/L oxalic acid and 0.2 mmol/L OS. The pH of the eluent was 3.3. At lower concentrations the electrochemical detection was somewhat improved because the metal ions were less complexed. However, the signals for cadmium, calcium and manganese were not resolved satisfactorily then. Higher concentrations led to a deterioration of the detection. The pH of the eluent was adjusted with ammonium hydroxide. Ammonium ions gave the lowest base currents, since their transfer is less facilitated by the ionophores than that of all other cations tested.

A chromatogram of a mixture of Pb^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+} and Ca^{2+} is shown in Fig. 1. Positive peak currents indicate, that cationic species are transferred from the aqueous to the organic phase. All metals were separated within 13 min. Mg^{2+} and Li^+ could be determined in the same chromatogram without interferences of the peaks. The dependence of the peak current on the potential difference between the reference electrodes in the aqueous and the organic phase is shown in Fig. 2. On the basis of this hydrodynamic voltammogram and the baseline of the chromatogram, the working potential was set to 320 mV. While Pb, Cd and Mn are transferred almost
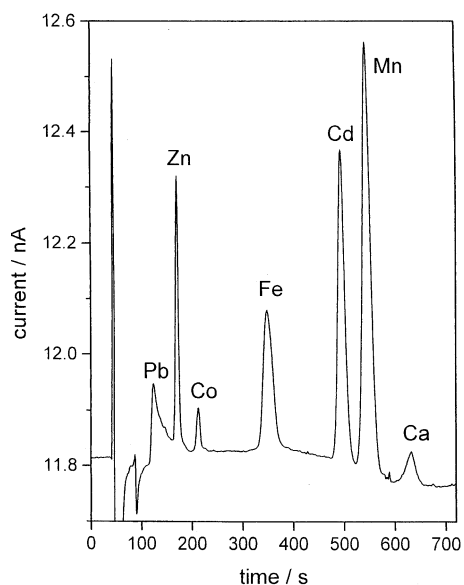

Fig. 1 Chromatogram of a standard solution containing Pb, Zn, Co, Fe, Cd and Mn (1 mg/L in each case). The peak for Ca is due to a contamination
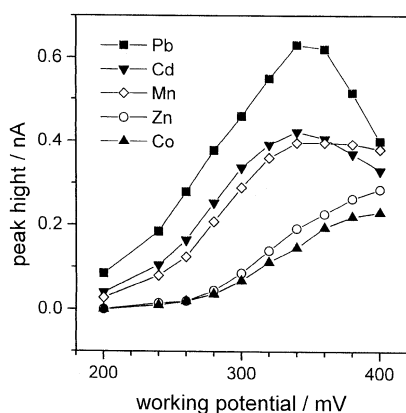
Fig. 2 Dependence of the peak height in the chromatogram on the working potential of the detector

conc. HNO_3 for 1 L sample) and filtered (cellulose acetate, 0.45 µm) before the injection. Samples with more than 1 mg (Zn)/L were diluted to be within of the calibration range. The results of the determination of Zn, Cd and Mn are compiled in Table 1 and 2. Atomic emission spectroscopy (ICP-AES) was used as reference method. While the results of both methods were practically in agreement for about the half of the data, too low values of the new method are found for the other part of the data. An explanation for this finding could be, that a part of the metal ions in the sample is not available for the electrochemical detection because of a strong bonding to the sample matrix. This problem will be subject to further studies. Another problem rises
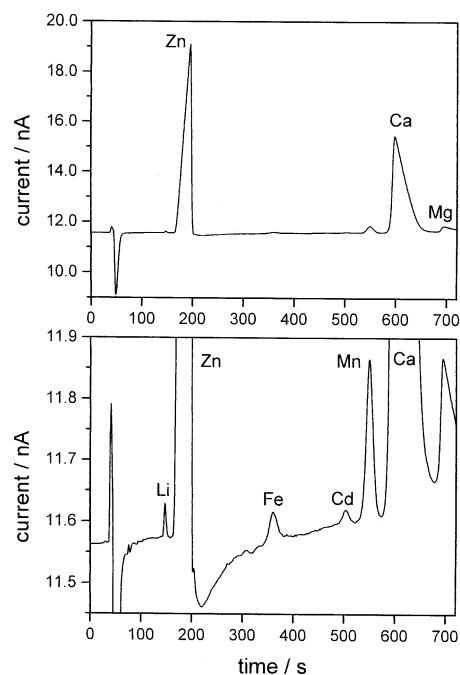
in the range of the limiting diffusion current, the current for Zn and Co is significantly below the limiting diffusion current. The dependence of the peak current on the concentration is linear as expected for the amperometric detection principle. The intercept of the calibration curve of Zn with the y-axis is above zero, this is probably due to an impurity in all standards. The limits of decision were determined from m = 5 concentration steps for each metal using a calibration curve method [24] (n = 3, m = 5, P = 0.95). Their estimates are 19(Pb^{2+}), 9(Zn^{2+}), 91(Co^{2+}), 8(Cd^{2+}) and 1.6 (Mn^{2+}) µg/L. The upper limit of the linear working range was about 2 mg/L (Co: 20 mg/L). A deflection of the calibration curves at higher concentrations can be attributed to the larger ohmic potential drop at higher currents.

The applicability of the method to real samples was investigated with water samples from an area with mining industry. The samples were taken at different sites or different days from two small brooks (no. 1–4), a drainage tunnel (no. 5 and 6) and a drainage ditch near a slack heap (no. 7 and 8). Sample 9 is a seep water from a slack heap. The samples were made acidic (1 mL

Fig. 3 Chromatogram of a seep water sample after dilution by a factor of 100 (the lower picture is a zoomed part of the upper one)

Table 1 Results of the determination of zinc in water samples from a mining area obtained with ion pair chromatography with electrochemical detection (IPC-ED) and plasma emission spectroscopy (AES-ICP)

Sample no.	1	2	3	4	5	6	7	8	9
AES-ICP	0.11	0.069	4.3	4.0	20.1	18.3	188	228	4120
IPC-ED	0.11	0.073	3.4	3.9	16.8	12.9	133	235	2860
% of AES-ICP	100	106	79	98	84	70	71	103	69

Table 2 Results of the determination of cadmium and manganese in water samples from a mining area obtained with IPC-ED and AES-ICP

Sample no.	7		9		10	
	AES-ICP	IPC-ED	AES-ICP	IPC-ED	AES-IPC	IPC-ED
[Cd]/mg/L	0.62	0.50	4.7	2.8	0.014	0.014
[Mn]/mg/L	2.3	3.8	28	22		

from the high calcium concentration present in many samples, leading to a strong overload of the separation column by calcium ions. This causes a very broad calcium peak, so that the determination of manganese or cadmium becomes impossible. To avoid the problem, separation columns of a higher capacity should be used. Since columns with an increased capacity would require stronger eluents, ionophores which exhibit a larger complex stability with the metals of interest must be found and are subject of present investigations. The use of new ionophores should also open the possibility to detect other metals, e.g. copper and nickel.

The chromatogram of a sample containing a very high content of several metals is shown in Fig. 3. Since the sample was diluted by a factor of 100, the peak of calcium was of satisfactory width and did not overlap with the signal of Mn or Cd in this chromatogram.

Conclusions

The applicability of a newly developed detector for the determination of metal ions in water samples using ion pair chromatography as a separation method has been demonstrated. Compared with AES-ICP, the findings were too small in some cases. The effect of a sample digestion should be investigated in the future, along with recovery experiments. Another important task is to find stronger ionophores. This would allow to use stronger eluents and columns of a higher capacity, so that an overload of the column can be avoided. Further, new ionophores should allow the determination of other metals, e.g. copper and nickel.

References

1. Koryta J (1991) Ion-selective Electrode Rev 13:133
2. Senda M, Kakiuchi T, Osakai T (1991) Electrochim Acta 36: 253–262
3. Wang E, Sun Z (1988) Trends Anal Chem 7:99–106
4. Yamamoto Y, Osakai T, Senda M (1990) Bunseki Kagaku 39:655
5. Krause J, Umland F (1989) Fresenius Z Anal Chem 335: 791–795
6. Wilke S, Franzke H, Müller H (1992) Anal Chim Acta 268: 285–292
7. Yamamoto Y, Nuno T, Osakai T, Senda M (1989) Bunseki Kagaku 38:589
8. Wang E, Liu Y (1986) J Electroanal Chem 214:459–465
9. Marecek V, Jänchenova H, Brezina M, Betti M (1991) Anal Chim Acta 244:15–19
10. Osborne MD, Girault HH (1995) Electroanalysis 7:714–721
11. Osborne MD, Girault HH (1995) Mikrochim Acta 117:175–185
12. Wang E, Ji H (1989) Electroanalysis 1:75
13. Weiss J (1985) Handbuch der Ionenchromatographie. VCH, Weinheim
14. Cassidy EM, Elchuk S (1982) Anal Chem 54:1558–1563
15. Pereira CM, Silva F (1994) Electroanalysis 6:1034–1039
16. Umetani S, Kihara S, Matsui M (1990) Anal Chim Acta 232:293
17. Yu W, Freiser H (1987) Anal Sci 3:401–403
18. Thomas DW, Foulkes–Williams C, Rumsby PT, Gower MC (1992) In: Fogarassy E, Lazare S (eds) Laser ablation of electronic materials. Elsevier, Amsterdam
19. Seddon BJ, Shao Y, Girault HH (1994) Electrochim Acta 39: 2377–2386
20. Hundhammer B, Wilke S (1989) J Electroanal Chem 266:133
21. Wilke S (1991) J Electroanal Chem 301:67
22. Issleib K, Baldauf L (1960) Pharmazeut Zentralhalle 99: 329–335
23. Yan D, Zhang J, Schwedt G (1989) Fresenius Z Anal Chem 335: 687–691
24. DIN 32645 (1994) Part I: Chemische Analytik; Nachweis-, Erfassungs- und Bestimmungsgrenze; Ermittlung unter Wiederholbedingungen; Begriffe, Verfahren, Auswertung, Beuth, Berlin