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**NEW VOLTAMMETRIC METHODS
FOR THE DETERMINATION OF HEAVY METALS
USING A MONTMORILLONITE MODIFIED
CARBON PASTE ELECTRODE**

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A carbon paste electrode modified with the clay mineral montmorillonite (MM) has been used to develop methods for the voltammetric determinations of cadmium(II), lead(II), copper(II) and mercury(II). The CPE has been modified by a newly developed procedure by direct mixing of the clay mineral, swollen in 1M KCl solutions for 12 hours and dried at 100 °C with the carbon paste. The analytical methods are based on the ion exchange properties of montmorillonite (MM). Methodological parameters such as pH of the analyte solution, preconcentration time and dependence of the voltammetric signal on the concentration of the analyte are investigated; the influence of interferences is studied. The detection limits (3σ) are 160 ng l⁻¹ for cadmium, 600 ng l⁻¹ for lead, 430 ng l⁻¹ for copper and 10 µg l⁻¹ for mercury(II) applying a preconcentration time of 10 minutes. To show the applicability of the methods, environmental samples are investigated. Another topic of the work presented

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here is to model preconcentration of divalent cations under open circuit conditions. The applicability of a model described by Kalcher et al. [1] is investigated with all ionic species in question. The results show that the congruence between experimental and modelled data is excellent. A comparison of equilibrium constants obtained from electrochemical experiments and calculated by the model and equilibrium constants obtained from batch experiments shows almost excellent correlation.

Introduction

Modified carbon paste electrodes have been used extensively in the field of electrochemistry [2]. Carbon paste as electrode material is particularly capable of being modified in a rather simple way. Clay minerals and zeolites have stimulated increasing interest due to their ion exchange capacity, molecular sieve selectivity, high thermal stability and resistance to extreme chemical conditions [3]. Clay minerals are naturally occurring efficient ion exchangers. They are crystalline, microporous materials, with charged surface groups. For modification of CPEs with clays these materials are usually swollen in pure water, dried in air, and then mixed with carbon paste [4].

Montmorillonite (MM), a clay mineral with distinctive ion exchanging properties, has been chosen as modifier in the present work.

The goal of the work presented was fundamental investigation into the adsorption of several selected heavy metals at the clay mineral *montmorillonite* with two aims: to develop analytical methods based on the ion exchange reaction between the clay surface and the analytes as well as to model preconcentration of divalent cations under open circuit conditions based on the model described by Kalcher et al. [1].

Experimental

Chemicals and Reagents

Deionized water was distilled twice in a quartz still and finally purified *via* a cartridge system (Nanopure, Barnstaed). Montmorillonite was purchased from Fluka (Montmorillonite KSF). All chemicals were of suprapure or analytical grade.

Apparatus

DPV and CV: The experiments were performed using a Par 264A polarograph (Princeton Applied Research) in combination with an automatically controlled

laboratory-built cell compartment made of Plexiglass [5]. The cell consisted of a 20–60 ml titration vessel of glass (Metrohm 6.1415.220) with a platinum wire as counter electrode and a saturated calomel electrode (SCE, Ingold 303-NS) as reference. The reference electrode was in contact with the supporting electrolyte via a salt bridge (1M KCl) with a vycor frit. The solution in the cell could be stirred with a Teflon-coated stirring bar. De-aeration of the solution was carried out with argon (99,999%, Messer Griesheim) for at least five minutes every time a new solution had been filled into the vessel. Argon was purged through the solution with a teflon tube. During the measurement argon was passed over the solution to avoid contact with oxygen.

Voltammetric curves were registered either on a compensograph (X-Y 1924, Siemens) and evaluated manually by the tangent fit method, or transferred to a personal computer after analogue-to-digital conversion by an appropriate interface [6].

Coulometry: Linear sweep measurements were carried out using a PAR 273 galvanostat (Princeton Applied Research) controlled with an IBM PS 2/H30 personal computer and corresponding software (M270, Princeton Applied Research) in combination with the same cell compartment as for DPV measurements. The charge involved in the electrode reaction was determined by integration of the LSV signal over time, which was performed automatically by the software.

Determination of equilibrium constants with AAS

500 mg of pre-treated montmorillonite KSF was suspended in 50 ml analyte solution containing definite concentrations of the heavy metal. The suspension was stirred for 12 hours. Then the suspension were centrifuged and the clear solutions were used for further measurements. The untreated stock solutions were acidified with nitric acid (final concentration 0.1 mol l^{-1}) and diluted to a concentration of 5 mg l^{-1} . Those stock solutions which were mixed with montmorillonite were also acidified and diluted in the same ratio as the untreated solutions. The concentration of the analyte in untreated and clay-treated solutions was determined with a flame atomic absorption spectrometer (model Z6100, HITACHI) with acetylene as fuel gas and air as oxidant. The amount of analyte exchanged into the clay was calculated from the decrease of the concentration of the species in solution. The decrease was evaluated from the ratio of the FAAS-signals after dilution of both solutions in the same ratio.

Determination of equilibrium constants with ICP-MS

The procedure of exposing mercury to the clay mineral was analogous to that procedure the other metals under investigation. For better comparison of the electrochemical equilibrium constant with the experimental constant, mercury

was exchanged under the same conditions as those of the voltammetric measurements. ICP-MS measurements were performed using a FISON Instrument Plasma Quad TurboII+ ICP-MS.

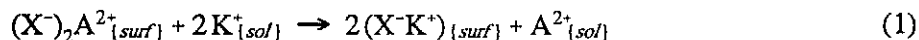
Preparation of the Modified Electrode

Montmorillonite KSF in its native form (10 g) was stirred with 100 ml 1M KCl solution (investigations with cadmium, copper and mercury) for 12 hours, and under similar conditions with 1M KNO₃ solution (investigations with lead). Then the suspension was filtered through a crucible with sintered disk (G2) and the *montmorillonite* was washed twice with water. The swollen clay was dried at 100 °C (after swelling in KCl) and 80 °C (after swelling in KNO₃) for 3 hours and stored over silica gel.

The carbon paste was prepared by thoroughly mixing 1.6 grams of spectral carbon powder with 400 mg swollen *montmorillonite* and adding 720 µl paraffin to the homogeneous mixture. The concentration of the modifier was 20% w/w with respect to the solid part of the paste and 15.2 % w/w to the entire material (specific mass 1.33 g ml⁻¹). As working electrode a laboratory built electrode was used which consisted of a Teflon rod (outer diameter 10 mm) with a 3 mm deep centric hole (diameter 7 mm) for the carbon paste filling and a platinum wire through the center of the rod for electric contact.

Procedure for Accumulation and Voltammetric Determination of Heavy Metals under Investigation

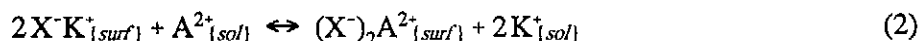
After recording the voltammogram, the electrode was rinsed with water and exposed to a well stirred (approximately 300 rpm) solution of potassium salts (1M) for 120 s. The concentration was sufficient for complete removal of adsorbed analyte according to Eq. (1); higher concentrations gave no improvement of reproducibility.



X⁻ exchanging site within the clay

A²⁺ analyte cation

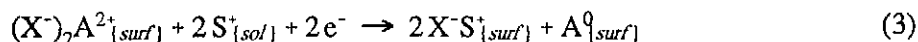
Thereafter the electrode was conditioned for 120 s, and after conditioning, it was exposed to the stirred analyte solution (20 ml) containing the analyte. Preconcentration of the analyte is based on ion exchange as described in Eq. (2)



Between all exchanges of medium, the electrode was rinsed with water for about

2 s. After exposure to the analyte solution for the required time, the electrode was removed, rinsed with water, placed into the voltammetric cell and connected to the polarograph. Voltammetric determinations were performed applying anodic stripping voltammetry. With this technique loss of accumulated analytes after their release by the cations of the supporting electrolyte is avoided.

Immediately after immersion of the electrode, negative potentials were applied for 15 s. During equilibration, preconcentrated analytes are reduced to the elemental states



S^{2+} supporting electrolyte

During the scan, the elemental analyte is reoxidized (Eq. (4)). The curve was monitored in differential pulse mode in anodic direction and the peak height was determined by the tangent fit method.



Table I summarizes the analytical scheme for the preconcentration and voltammetric determination of the heavy metals under investigation.

Table I Analytical scheme for preconcentration and voltammetric determination of cadmium, lead, copper and mercury using a montmorillonite modified carbon paste electrode

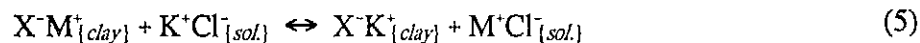
	Cadmium	Lead	Copper	Mercury
Regeneration	1M KCl	1M KNO ₃ , 2.5×10 ⁻⁴ M HNO ₃	1M K ₂ SO ₄	1M KCl
Conditioning	H ₂ O	2.5×10 ⁻⁴ M HNO ₃	H ₂ O	0.01M NH ₃ 0.05M NH ₄ NO ₃
Accumulation	H ₂ O	2.5×10 ⁻⁴ M HNO ₃	H ₂ O	0.01M NH ₃ 0.05M NH ₄ NO ₃
Supporting Electrolyte	0.075M NH ₄ Cl	0.1M KCl, 10 ⁻³ M HCl	0.1M KCl 0.05M HCl	0.1M NH ₄ SCN 0.01M HCl ₄

Results and Discussion

Pre-Treatment of MM and Modification of the CPE

Like all clay minerals *montmorillonite* changes its interlayer spacing on contact with aqueous solutions. Therefore, this compound cannot be introduced into the carbon paste in dehydrated conformation but has to be swollen in aqueous

solutions before modification of the electrode by direct mixing. In literature pretreatment of clay minerals for their use as modifiers for electroanalytical investigations is usually performed by swelling the clay in water for a certain period of time and drying it by suction. In this case the modifier in the paste contains about 20% water. This procedure includes some disadvantages concerning the analytical performance of the modified electrode: the ion exchange capability of the clay is usually diminished since for a complete ion exchange capacity all exchanging sites of the clay have to be saturated with easy removable cations (activation of the electrode). The percentage of water within the clay mineral strongly depends on experimental parameters and on the way of removing excess water. In this work, montmorillonite was swollen in electrolyte solutions (KCl, KNO₃), washed with water and dried at temperatures between 80 and 100 °C. The swelling process in electrolyte solutions was monitored by laser microprobe mass analysis (Lamma). The spectra show that the clay mineral is extensively loaded with potassium ions, whereas no significant sorption of the corresponding anion of the electrolyte can be observed. This behaviour can be explained by the fact, that clay minerals predominantly act as cation exchangers. The sorption of potassium ions during the swelling process can be expressed by equation



M⁺ alkali metal cations, H⁺

To compare the analytical performance of the *MM*-modified electrode pre-treated in our original way with that of an electrode modified in a way taken from literature, cadmium(II) was accumulated under open circuit conditions at both types of modified electrodes. Figure 1a shows cyclic voltammograms of cadmium after external accumulation of 1 mg l⁻¹ Cd(II) for 120 s. Curve (I) displays the cyclic voltammogram using *montmorillonite* swollen in 1M KCl for 12 hours and curve (II) is obtained after swelling it in water for 5 hours. In anodic direction a re-oxidation peak is visible at a potential of -0.78 V vs. SCE, in cathodic direction reduction of cadmium to the elemental state can be observed at a potential of -1 V vs. SCE. The anodic current response clearly indicates that a solution of potassium chloride is more effective for swelling than water alone. In the differential pulse anodic stripping mode the difference between both types of modified electrodes becomes even more visible. Figure 1b shows differential pulse voltammograms of cadmium(II) using CPEs modified with *montmorillonite* swollen in 1M KCl for 12 hours (curve II) and after swelling it in water for 5 hours (curve I). Again it can be seen that the swelling procedure with KCl yields higher current responses. The background currents are nearly equal for both swelling procedures indicating that KCl does not have a deteriorating effect in this respect.

General

All species under investigation show good affinity towards montmorillonite and can be preconcentrated under open circuit conditions without application of a potential. The accumulation process is dominated by an ion-exchange reaction. On the other hand, these analytes cannot be preconcentrated at an unmodified CPE since no significant electroactivity can be observed after preconcentration under open circuit conditions.

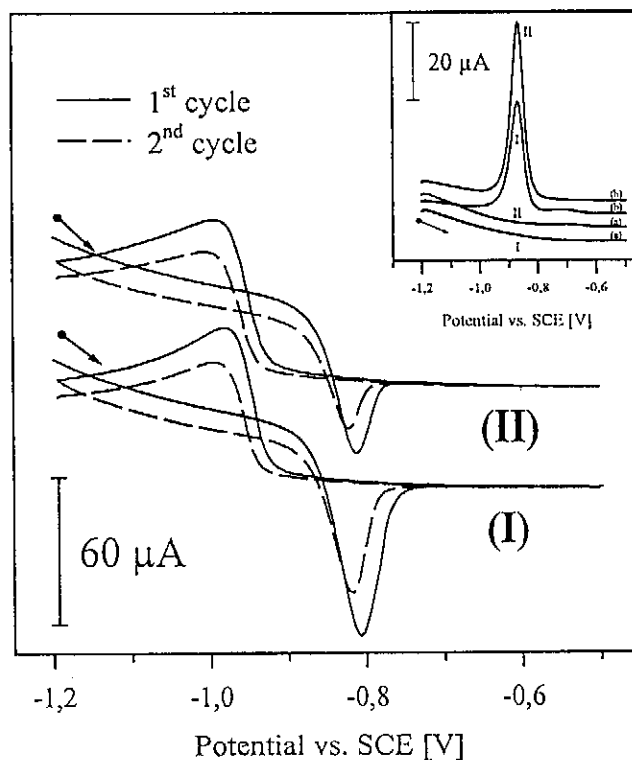


Fig. 1 A) Cyclic voltammograms of cadmium using *montmorillonite*-modified carbon paste electrodes: (I) *montmorillonite* swollen in 1M KCl for 12 hours, (II) swollen in H₂O for 5 hours; supporting electrolyte 0.075M NH₄Cl; analyte solution 1 mg l⁻¹ Cd(II); accumulation time 120 s; scan rate 20 mV s⁻¹; 15,2 % w/w *montmorillonite* in the paste.

B) Differential pulse voltammograms of cadmium(II) using *montmorillonite* modified carbon paste electrodes: (I) *montmorillonite* swollen in water for 5 hours; (II) *montmorillonite* swollen in 1M KCl for 12 hours, dried at 100 °C; (a) blank; (b) 200 μ g l⁻¹ Cd(II); supporting electrolyte 0.075M NH₄Cl; accumulation time 120 s; scan rate 10 mV s⁻¹; 15.2 % w/w *montmorillonite* in the paste

Voltammetric Characterization of Cadmium(II)

Figure 2 shows the behavior of a clay-modified electrode towards open circuit accumulation of cadmium. No electrochemical reactions occur at the unloaded electrode in the potential range between $-1,2$ V and $-0,5$ V vs. SCE. Cd^{2+} accumulated under open circuit conditions gives a large and well defined re-oxidation peak at a potential of $-0,78$ V vs. SCE in the cyclic voltammogram. Repetitive cycles show a gradual decrease of this signal which is caused by migrations of cadmium(II) ions into the bulk solution. Therefore, starting voltammetric scans at negative potential and scanning in anodic direction is preferable because loss of accumulated cadmium is prevented by its reduction to the elemental state. In the reversed scan Cd^{2+} , which is still immobilized in the clay, is reduced to its elemental state at about $-1,0$ V vs. SCE. The potential shift between reduction (slightly overlapped with hydrogen evolution) and re-oxidation can be ascribed to a somewhat irreversible electrode reaction as well

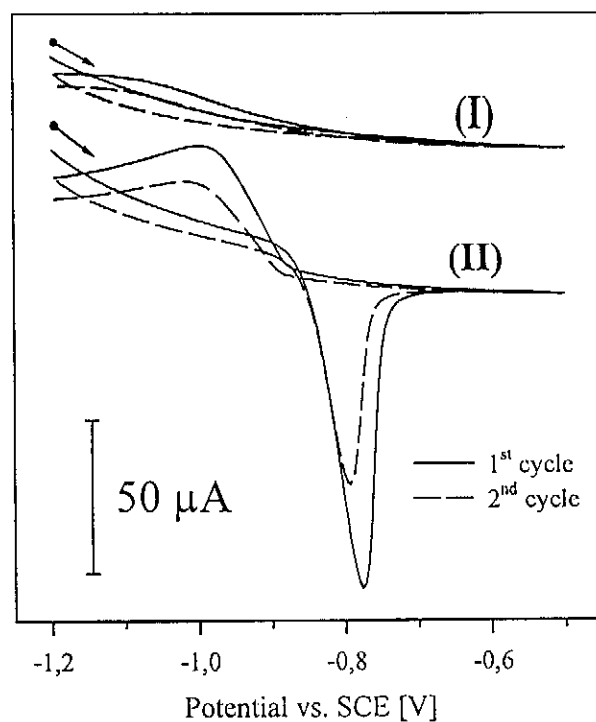


Fig. 2 Cyclic voltammograms of cadmium(II) accumulated at a *montmorillonite*-modified carbon paste electrode under open circuit conditions; (I) blank; (II) after exposure to a solution containing 2.5 mg l^{-1} Cd(II) ; supporting electrolyte: $0.075\text{M NH}_4\text{Cl}$; accumulation time: 120 s ; scan rate 20 mV s^{-1}

as to non ideal behaviour of carbon paste for electron transfers. During repetitive scans, the re-oxidation peak is slightly shifted towards more negative potentials between the 1st and 2nd cycles, and then it remains constant. The reason could lie in the fact that after the first cycle all the Cd^{2+} is immobilized after re-oxidation in direct vicinity of the carbon particles; as a consequence, effective diffusion is quicker so that re-oxidation takes place virtually more easily.

Voltammetric Determination of Cadmium

Cadmium can be preconcentrated at a *montmorillonite*-modified CPE under open circuit conditions. From cyclic voltammetric investigations it is obvious that anodic stripping voltammetry is preferable due to better exploitability of the signals, easier regeneration of the electrode and prevention of losses of the accumulated analyte during the voltammetric scan (Fig. 3).

Optimization of the analyte solution showed two maxima, one at pH 3–4 and the other at pH 7. This indicates that probably two different mechanisms of sorption operate. At pH around 6, cadmium is exchanged as cation. This opti-

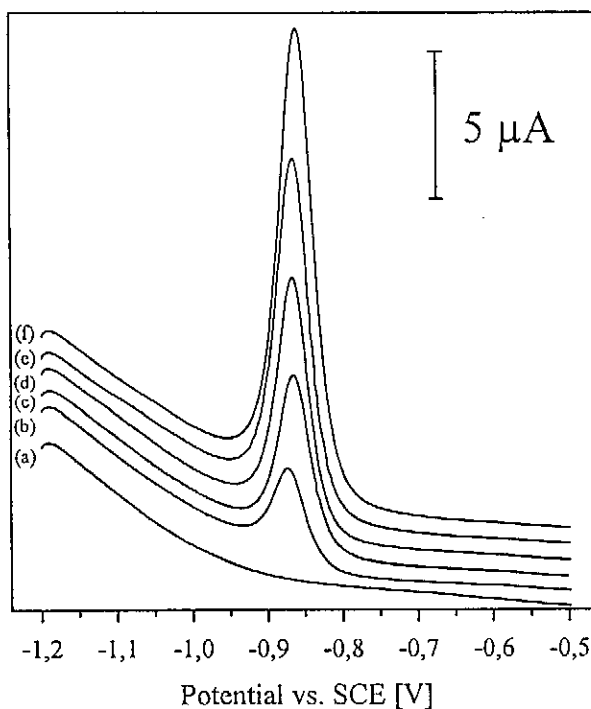


Fig. 3 Differential pulse voltammograms of cadmium(II) using a *montmorillonite*-modified carbon paste electrode; supporting electrolyte: 0.075M NH_4Cl ; accumulation time 120 s; (a) blank, (b) 40 $\mu\text{g l}^{-1}$ Cd(II), (c) 80 $\mu\text{g l}^{-1}$ Cd(II), (d) 120 $\mu\text{g l}^{-1}$ Cd(II), (e) 160 $\mu\text{g l}^{-1}$ Cd(II), (f) 200 $\mu\text{g l}^{-1}$ Cd(II)

mum is identical with the point of zero charge which is at pH 6.1 [7]. This optimum is additionally favored by the matrix, which has rather low concentration of other concurring ions. At pH values larger than 7.5, hydrolysis of cadmium occurs and decreases the extent of accumulation. The smaller maximum at lower pH can probably be ascribed to additional preconcentration of CdCl_4^{2-} anions at positively charged exchange sites. At pH 2 the concentration of hydronium ions is large enough to compete for the ion exchanging sites in the clay.

To support the presumption that cadmium is also accumulated as CdCl_4^{2-} at pH 3.6, sodium chloride was added to the analyte solution at different pH values. In acidic medium the presence of chloride in the test solution favours the CdCl_4^{2-} complex formation. At pH 3.6 an increase of the accumulated amount of cadmium up to a concentration of $2 \times 10^{-3} \text{ mol l}^{-1}$ sodium chloride added to the analyte solution can be observed, whereas with higher NaCl concentrations competitive ion exchange occurs for positively and negatively charged sites yielding lower currents. At notably higher pH values the signal current decreases exponentially with increasing sodium concentration, which indicates the competitive replacement of cadmium by the sodium cation.

The investigation dealing with the dependence of the DPV signal on the preconcentration time for various concentrations of cadmium showed that with small concentrations the time dependence is sigmoidal for short periods. This behaviour was also found by Wang and Martinez [8] for the accumulation of silver at a zeolite-modified carbon paste electrode. The reason for a smaller increase with short periods than expected may be in the fact that the ion exchange is not restricted to the interface only but that also migration of the electroactive species into a certain depth of the surface occurs. Thus the expected exponential increase of current with time is overlapped by a delay effect caused by diffusion of the analyte into the paste. With longer preconcentration times and higher concentrations of the analyte, migrational effects are not visible in the graphs anymore.

In contrast to many articles about voltammetric determinations of cations using clay- and zeolite-modified carbon paste electrodes, deviations from the linear dependence of the voltammetric signal on the preconcentration time were observed after a relatively long period of about 45 minutes. Wang and Martinez investigated the preconcentration of silver at a zeolite-modified CPE and found that the limiting current is achieved after 8 to 10 minutes. Also Hernandez found a similar behaviour for mercury with a zeolite-modified CPE [9].

One reason for the longer range of linear dependence of the analyte signal on the accumulation time may lie in the different pre-treatment of the clay. For all reported studies the clay or zeolite was incorporated in the paste in its air dried form after swelling in pure water. This procedure does not fully activate all the exchanging sites of the clay. As a consequence, the amount of functional groups at the electrode surface is very small and, therefore, equilibrium is reached rather soon. Swelling of the clay in an electrolyte such as potassium

chloride leads to different interlayer distances in the clay and to increased accessibility of ion exchanging sites. Availability of a much larger amount of functional groups also in the interior of the clay explains the long range of linear dependence of the cadmium signal height on the preconcentration time.

The dependence of the voltammetric peak height on the concentration of cadmium(II) is shown in Fig. 4. All graphs display linear curves within the given concentration range. With proper preconcentration periods, determinations of cadmium(II) from 1 to 500 $\mu\text{g l}^{-1}$ Cd(II) are possible. With an accumulation time of 10 minutes, still applicable for routine analysis, the lowest achievable limit of detection is about 200 ng l^{-1} Cd(II) (3σ value of the peak heights with a cadmium concentration near the detection limit).

The relative standard deviation of the voltammetric signal for a concentration of 20 $\mu\text{g l}^{-1}$ cadmium with a preconcentration time of 5 minutes is 4.0 % for 5 repetitive measurements. For concentration over 50 $\mu\text{g l}^{-1}$ cadmium the average relative standard deviation is around 3 %.

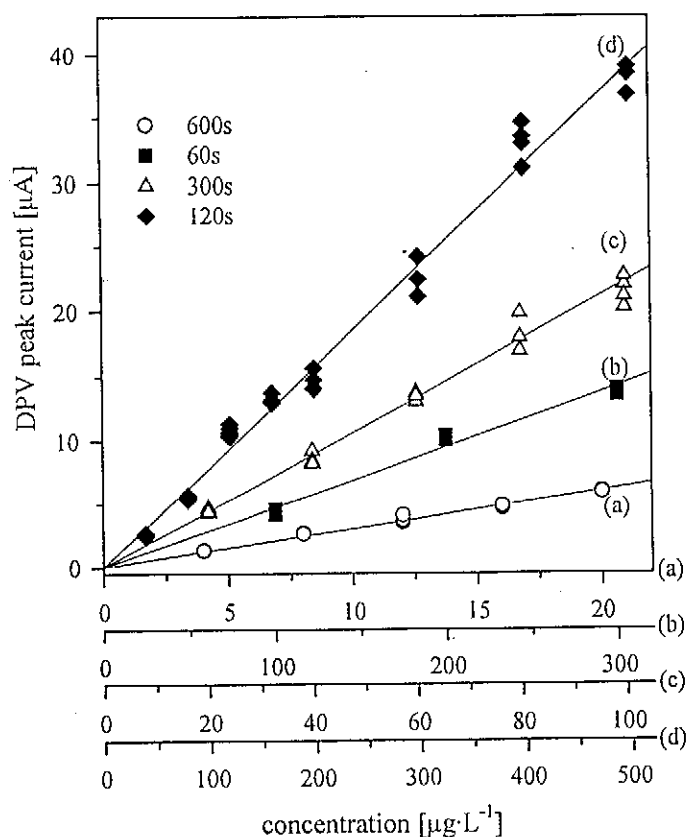


Fig. 4 Dependence of the DPV peak height on the Cd(II) concentration in the analyte solution: supporting electrolyte: 0.075M NH_4Cl ; preconcentration time (a) 600 s, (b) 60 s, (c) 300 s, (d) 120 s

Though *montmorillonite*, like all clay minerals, does not exhibit any specific selectivity towards cations, exclusion reactions determine the extent of interference. Charge and size of the hydrated species and their ability to penetrate the clay layer determine the degree of competitive displacement of cadmium. Therefore, those species are interesting which are known to be electroactive in the same potential range as cadmium(II). For investigations, interferents were added in a five and fifty fold mass excess of cadmium (Table II).

Table II Change of DPV peak current caused by interfering cations in the analyte solution: analyte solution: $100 \mu\text{g l}^{-1}$ Cd(II); supporting electrolyte: $0.075\text{M NH}_4\text{Cl}$; accumulation time 120 s

Interferent	Added as	Change of peak current [± %]		Remarks
		Concentration of interferent		
		$500 \mu\text{g l}^{-1}$	$5000 \mu\text{g l}^{-1}$	
Zn ²⁺	ZnCl ₂ /H ₂ O	+24.1	+17.3	
Tl ³⁺	TlCl ₃ /0.01M HCl	+68.5	+1700	(a)
Tl ⁺	Tl ₂ SO ₄ /H ₂ O	+201	+1900	(a)
Sn ⁴⁺	SnCl ₄ /1 M HCl	+7.7	+11.8	
Sn ²⁺	SnCl ₂ /1 M HCl	+10.5	-35.1	
Pb ²⁺	Pb(NO ₃) ₂ /0.001 M HNO ₃	-42.6	-52.2	
Cu ²⁺	CuCl ₂ ·H ₂ O/H ₂ O	-100	-100	(b)

Remarks: (a) overlap of peaks, no discrimination possible
(b) no exploitable cadmium signal.

To prove the applicability of the analytical method it was used to determine cadmium(II) in municipal waste water of Graz. The filtered sample (pretreated with H₂SO₄ and UV radiation) had a concentration of $9.64 \pm 0.25 \mu\text{g l}^{-1}$ cadmium; the value was verified by graphite furnace atomic absorption spectrometry (Gfaas) yielding $9.19 \pm 0.25 \mu\text{g l}^{-1}$ cadmium. Both methods give results which are in good agreement of the mean values and the same standard deviation. Although the sample contains a lot of interfering species (alkali metals, heavy metals) the voltammetric determination of cadmium using the *montmorillonite*-modified carbon paste electrodes is possible with sufficient accuracy.

Voltammetric Characterization of Lead

Similar to cadmium lead can be preconcentrated at a montmorillonite- modified carbon paste electrode under open circuit conditions. Figure 5 displays the cyclic voltammograms of lead(II) accumulated at a modified carbon paste electrode under open circuit conditions. The blank shows a broad signal up to a potential of about -0.6 V vs. SCE for the anodic scan and at < -0.75 V for the cathodic run. The nature of these current responses is unclear; presumably reduction of adsorbed oxygen as well as of hydronium ions may be the reason. After accumulation of lead(II) a sharp re-oxidation peak at -0.54 V vs. SCE is observed. During repetitive scans its potential shifts 10 mV to more negative values similar to cadmium. The electrode reaction is irreversible, and the reduction signal of lead is overlapped by the hydrogen wave. Evidently it is not exploitable for analytical purposes.

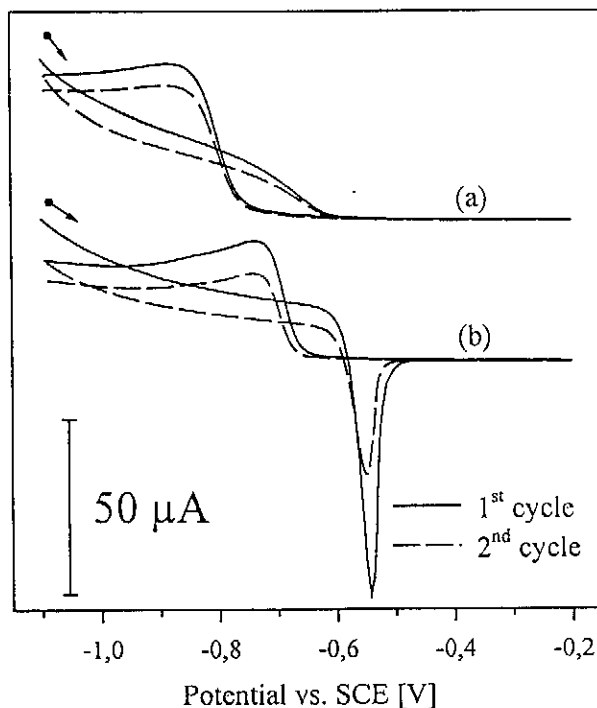


Fig. 5 Cyclic voltammogram of lead(II) using a *montmorillonite*-modified carbon paste electrode: (I) blank; (II) 1 mg l^{-1} Pb(II) accumulated under open circuit conditions; supporting electrolyte: 0.1 M KCl , 10^{-3} M HCl ; analyte solution: $2.5 \times 10^{-4} \text{ M HNO}_3$; accumulation time: 120 s ; scan rate 20 mV s^{-1}

Due to the sharp re-oxidation signal of lead and the reasons mentioned before, DPASV was applied for quantitative determinations of lead. Figure 6 displays differential pulse anodic stripping voltammograms of various bulk concentrations of lead. The signals are superimposed on a small wave between -0.7 V and -0.5 V vs. SCE. In spite of this the signals are well defined and their height is easy to evaluate.

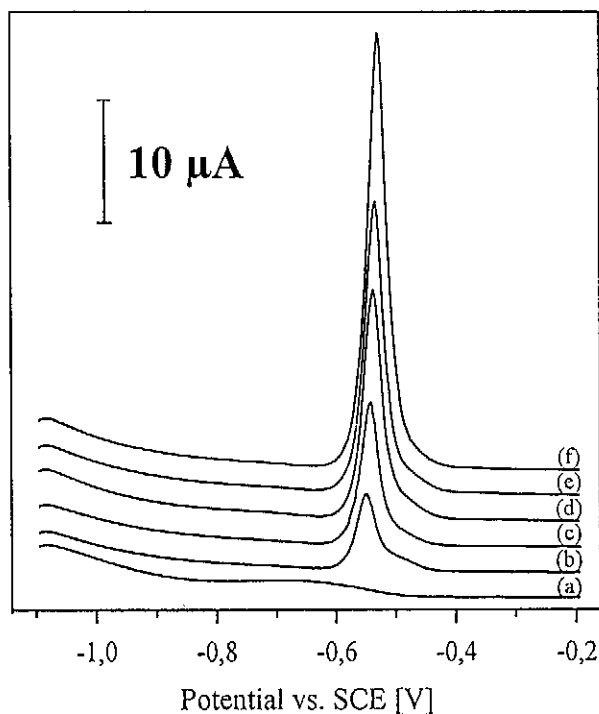


Fig. 6 Differential pulse voltammograms of lead(II) using a *montmorillonite*-modified carbon paste electrode: supporting electrolyte: 0.1M KCl , 10^{-3} M HCl ; accumulation time 120 s ; analyte solution $2.5 \times 10^{-4}\text{ M HNO}_3$, (a) blank, (b) $25 \mu\text{g l}^{-1}\text{ Pb(I)}$, (c) $50 \mu\text{g l}^{-1}\text{ Pb(II)}$, (d) $75 \mu\text{g l}^{-1}\text{ Pb(II)}$, (e) $100 \mu\text{g l}^{-1}\text{ Pb(II)}$, (f) $150 \mu\text{g l}^{-1}\text{ Pb(II)}$

Optimization studies dealing with the dependence of the voltammetric current on the pH of the analyte solution showed that in contrast to cadmium(II) the maximum current can be recorded when the pH value is around 3.5, whereas at pH 7 the response is very small. This may be due to the fact that in neutral medium lead ions already hydrolyze. At pH values below three the high concentration of hydronium ions blocks the ion exchanging groups; this effect is more pronounced when using more acidic media. The dependence of the peak height on the accumulation time was studied with various concentrations of

lead(II) in the analyte solution. The graphs are similar to those of cadmium. Again equilibrium conditions are reached with preconcentration times significantly longer than 10 minutes.

Calibration curves were established for various concentration ranges of lead(II) in the analyte solution applying proper accumulation periods (Fig. 7). Low concentrations of Pb^{2+} in combination with short preconcentration times usually yield voltammetric currents which are smaller than expected. The reason for this may be found in the fact that the dependence of the signal on the accumulation time is not linear with short periods due to migrational effects. Additionally, evaluation of small peak heights causes larger errors because the blank response is not negligible any more and the reoxidation signal of lead is superimposed on it.

Acceptable precision of linear dependence of the current on the concentration of Pb^{2+} can be achieved for a concentration range of about 1 to $500 \mu g l^{-1}$ lead. The detection limit (3σ) with a preconcentration time of 10

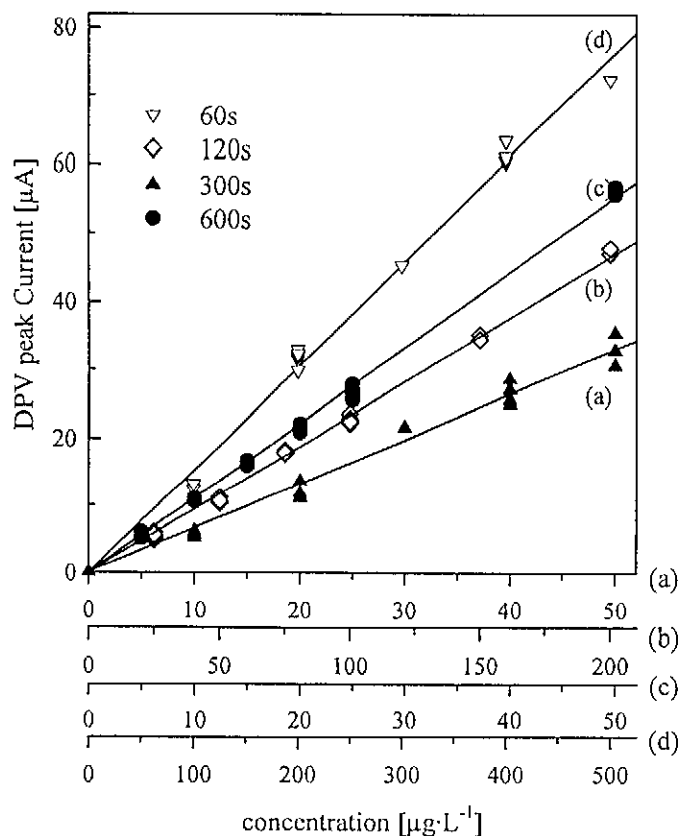


Fig. 7 Dependence of the DPV peak current on the concentration of lead(II) in the analyte solution: supporting electrolyte: 0.1M KCl, 10^{-3} M HCl; analyte solution: 2.5×10^{-4} M HNO_3 ; preconcentration time (a) 300 s, (b) 120 s, (c) 600 s, (d) 60 s

minutes is $0.60 \mu\text{g l}^{-1}$.

The ionic species which are expected to interfere with the voltammetric determination of lead were investigated (Table III). With exception of copper(II) all the species studied, which are electroactive within the same potential range as lead(II), influence the voltammetric determination of Pb^{2+} only moderately when applying the standard addition method. Particularly mercury can be present in significant excess without disturbing severely. Thallium, titanium and cadmium are tolerable to a 20 fold mass excess. The presence of copper in the analyte solution is, as in the case of cadmium, disastrous even in slightly higher concentrations than lead. Potassium sulfate does not interfere notably as long as the solubility product is not fallen short of.

The applicability of the described method for the voltammetric determination of trace amounts of lead(II) using a montmorillonite- modified carbon paste electrode was tested. Drinking water was spiked with $10 \mu\text{g l}^{-1}$ Pb(II) . The sample was used for voltammetric measurements without further treatment. The concentration of lead(II) in the sample was found to be $9.75 \pm 0.53 \mu\text{g l}^{-1}$ giving a recovery rate of 97.5%. To prove the results obtained with

Table III Change of DPV peak current caused by interfering species: analyte solution: $100 \mu\text{g l}^{-1}$ Pb(II) , accumulation time 120 s; supporting electrolyte: 0.1M KCl, 10^{-3} M HCl

Interferent	Added as	Change of peak current [±%]		Remarks
		Concentration of interferent		
		$500 \mu\text{g l}^{-1}$	$5000 \mu\text{g l}^{-1}$	
Tl^{3+}	$\text{TlNO}_3/\text{H}_2\text{O}$	+39.8	+64.4	
Ti^{4+}	$\text{TiCl}_4/5 \text{ M HCl}$	-38.4	-87.4	(a)
Cd^{2+}	$\text{CdCl}_2/\text{H}_2\text{O}$	+6.9	-76.8	(a)
Cu^{2+}	$\text{CuCl}_2 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}$	-100	-100	(a), (b)
Hg^{2+}	$\text{Hg(NO}_3)_2/0.01 \text{ M HNO}_3$	+1.7	-12.1	

Interferent	Added as	Change of peak current [±%]		Remarks
		Concentration of interference		
		5 mg l^{-1}	50 mg l^{-1}	
SO_4^{2-}	$\text{K}_2\text{SO}_4/\text{H}_2\text{O}$	-4.1	-13.9	

Remarks: (a) overlap of peaks, no discrimination possible
(b) no exploitable lead signal.

the modified carbon paste electrode, the concentration of lead in the sample was also determined with a hanging mercury drop electrode yielding a value of $9.89 \pm 0.3 \mu\text{g l}^{-1}$. Both results are in good agreement with respect to the mean value and the standard deviation.

Voltammetric Characterization of Copper

Copper can be preconcentrated at a montmorillonite- modified carbon paste electrode under open circuit conditions *via* an ion-exchange mechanism. Figure 8 displays cyclic voltammograms of copper(II) accumulated under open circuit conditions. The blank curve shows no significant signal beside a small broad wave in a potential range from -0.4 V to $+0.1 \text{ V}$ vs. SCE decreasing with further scans. After accumulation of copper(II) a sharp re-oxidation peak at -0.18 V vs. SCE can be observed. With repetitive scans the peak potential of this signal shifts 10 mV to more negative values. This behaviour was already observed with cadmium(II) and lead(II). Replacement of copper(II) ions by ions from the supporting electrolyte is indicated by the decrease of the voltammetric signals during repetitive cycling of the electrode. The second re-oxidation signal observable in the voltammogram arises at a potential of $+0.12 \text{ V}$ vs. SCE. The electrode reaction is irreversible; small reduction signals between -0.4 V and -0.65 V vs. SCE are assignable to the reduction of copper(II) to the elemental form (Fig. 8). The reduction signal is of poor quality and therefore not exploitable for analytical purposes. For these reasons differential pulse anodic stripping voltammetry was used for quantitative determinations of copper (Fig. 9). The shapes of peaks between 0.0 and $+0.2 \text{ V}$ vs. SCE show complex electrode reactions where the virtual overlap of oxidation and reduction is very typical of catalytic processes.

Voltammetric Determination of Copper

Several supporting electrolytes were investigated with respect to signal height and separation of the re-oxidation signals. Perchlorates of alkali metals yielded poor separation of both peaks, due to an anodic shift of the re-oxidation signal. This indicates that complexation of Cu^{2+} occurs to some extent. Also, oxidation of chloride to chlorine can be excluded as the reason for the second peak.

Chlorides and bromides of monovalent cations yield the best results, where particularly chlorides produce the highest signals. The potential of the oxidation of copper is also dependent on the concentration of chloride in the supporting electrolyte, again indicating at least slight complexation of Cu^{2+} . The peak potential shifts to more negative values with increasing chloride concentrations and remains constant above $0.075 \text{ mol l}^{-1} \text{ Cl}^-$. The cation of the supporting electrolyte also influences the height of the DPV signal. Lithium and

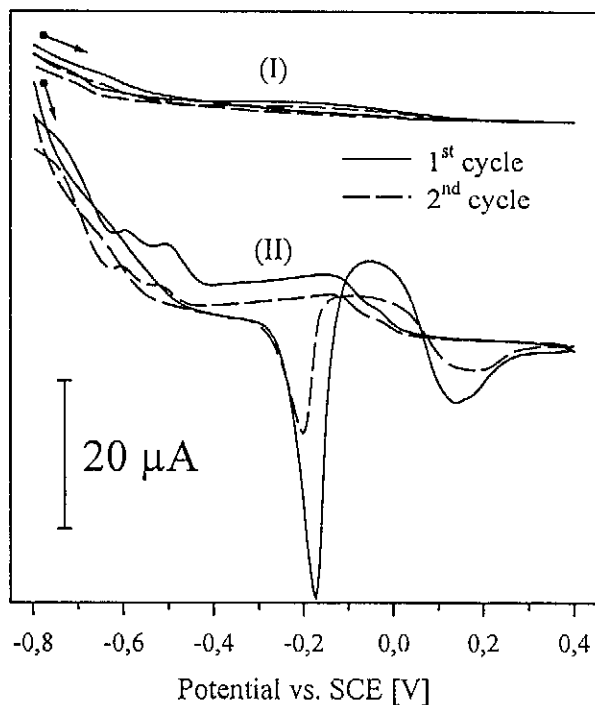


Fig. 8 Cyclic voltammograms of copper(II) using a *montmorillonite* modified carbon paste electrode: (a) blank; (b) 2.5 mg l^{-1} Cu(II) accumulated under open circuit conditions; supporting electrolyte: 0.1 M KCl , 0.05 M HCl ; accumulation time: 120 s ; scan rate 20 mV s^{-1}

sodium yield smaller peaks than potassium or ammonium, the latter two being practically identical. From this it may again be concluded that replacement of sorbed copper must precede its electrochemical reduction, a process, which is more effectively executed by K^+ and NH_4^+ . Investigations into the influence of the pH of the supporting electrolyte showed that the optimum concentration of hydrochloric acid is 0.05 mol l^{-1} .

In contrast to previous studies dealing with the determination of cadmium and lead, the signal height is rather independent of pH of the analyte solution in the range from 3 to 6. At lower pH values than three the large concentration of hydronium ions blocks the ion-exchanging groups of the clay. In alkaline medium copper hydrolyzes if the pH is adjusted with NaOH or KOH. In order to investigate the accumulation behavior of copper(II) in neutral and slightly alkaline media, an ammonia/ammonium buffer was used as matrix of the analyte solution. Ammonia is known to form a stable tetramine complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ if the concentration of NH_3 is sufficiently high. At pH 7, only small signals can be observed which may be caused by precipitation of $\text{Cu}(\text{OH})_2$. The maximum currents occur at pH 8 to 8.5 where all the copper is

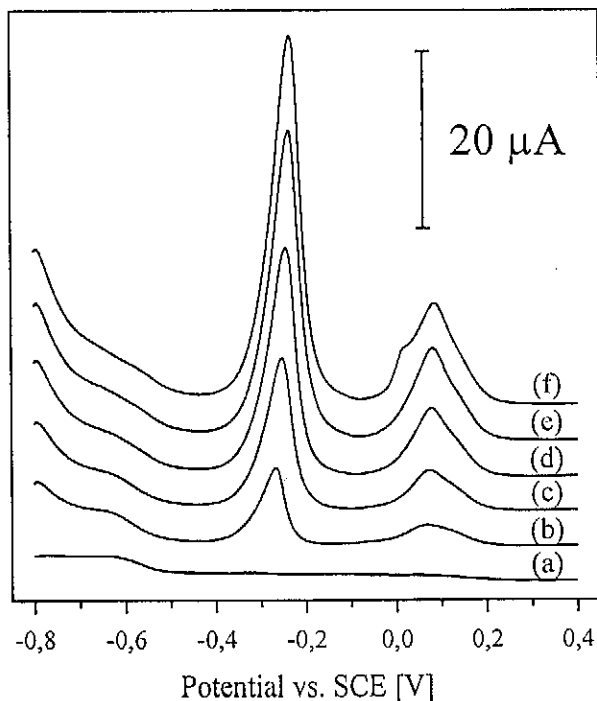


Fig. 9 Differential pulse voltammograms of copper(II) using a *montmorillonite*-modified carbon paste electrode: supporting electrolyte: 0.1M KCl, 0.05M HCl; accumulation time: 120 s; scan rate 10 mV s⁻¹; analyte solution: (a) blank, (b) 100 µg l⁻¹ Cu(II), (c) 200 µg l⁻¹ Cu(II), (d) 300 µg l⁻¹ Cu(II), (e) 400 µg l⁻¹ Cu(II), (f) 500 µg l⁻¹ Cu(II)

present as $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Increasing the pH obviously also decreases the amount of exchangeable groups in the *montmorillonite*, accompanied with an increasing concentration of ammonium ions which act as competitor for copper. The maximum current found in alkaline medium is still lower than in acidic solution at comparable concentrations.

The kinetics of the accumulation process of copper with respect to accumulation time is similar to those of cadmium(II) and lead(II), the limiting currents for long periods differ somewhat according to the affinity to the clay mineral.

For investigations about the dependence of the voltammetric current on the concentration of copper in the analyte solution, calibration curves were established applying suitable preconcentration periods (Fig. 10). Similarly to the former investigations dealing with cadmium and lead, small negative deviations from the strictly linear dependence can be observed at small concentrations of copper in combination with short accumulation times. In the case of copper, this deviation is less pronounced than with cadmium or lead. The calibration curves show linear dependence of the current on the Cu^{2+} concentration in a range of

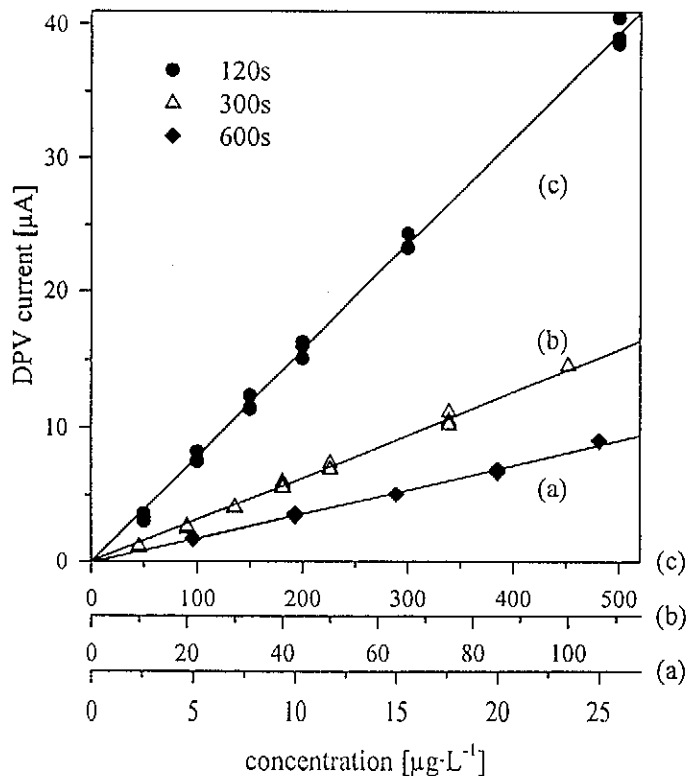


Fig. 10 Dependence of the DPV peak current on the concentration of copper(II) in the analyte solution: supporting electrolyte: 0.1M KCl, 0.05M HCl; accumulation time: (a) 600 s, (b) 300 s, (c) 120 s

5 to 500 $\mu\text{g l}^{-1}$ copper. The detection limit based on 3σ applying a preconcentration time of 10 minutes is 430 ng l^{-1} .

We have investigated ions which are expected to interfere with the voltammetric determination of copper due to overlap of signals. The results are summarized in Table IV. The presence of higher concentrations of silver ions in the analyte solution is disastrous. Silver produces a re-oxidation signal in the DPASV scan, more positive than copper, so that direct overlap of the signals is not the main problem. The destructive effect is mainly due to the formation of an intermetallic between silver and copper, where silver in excess forms some kind of plated film electrode. Thus the response of copper is severely interfered. The presence of Fe^{3+} in excess should be avoided. All other ions, which are electroactive in the same potential range as copper, interfere only moderately so that determinations are possible when applying the internal standard addition method.

The method for the voltammetric determination of copper(II) using a *montmorillonite*-modified carbon paste electrode was applied to municipal

Table IV Change of DPV peak current caused by interfering species: analyte solution: $100 \mu\text{g l}^{-1}$ Cu(II), accumulation time 120 s; supporting electrolyte: 0.1 M KCl, 0.05 M HCl

Interferent	Added as	Change of peak current [$\pm\%$]	
		Concentration of interferent	
		$500 \mu\text{g l}^{-1}$	$5000 \mu\text{g l}^{-1}$
Hg ²⁺	Hg(NO ₃) ₂ /0.1 M HNO ₃	+13.3	-20.0
Ag ⁺	AgNO ₃ /0.5 M HNO ₃	-76.7	-100
Fe ³⁺	FeCl ₃ /6 M HCl	+6.9	-76.8

waste water from Graz. The filtered sample was pretreated with HNO₃ and UV radiation; the concentration of copper in this sample was found to be $18.3 \pm 1.9 \mu\text{g l}^{-1}$. This value was verified applying DPASV using a hanging mercury drop electrode which gave a value of $17.9 \pm 1.2 \mu\text{g l}^{-1}$. Both results are in good agreement as far as the mean value and the standard deviation are concerned.

Voltammetric Characterization of Mercury

The cyclic voltammogram of mercury(II) after accumulation under open circuit conditions using a *montmorillonite*-modified carbon paste electrode is sketched in Fig. 11. The blank curve shows no significant current responses in the potential range from -0.8 to $+0.2$ V vs. SCE. After accumulation of mercury an oxidation signal is observed in the anodic scan at a potential of -0.05 V vs. SCE. The electrode process is strongly irreversible since only a small reduction signal at -0.3 V vs. SCE is visible. For analytical purposes the re-oxidation of Hg⁰ \rightarrow Hg²⁺ was exploited (Fig. 12).

Voltammetric Determination of Mercury

In contrast to the other heavy metals investigated in this work, mercury cannot be preconcentrated from acidic aqueous solutions since it forms negatively charged complexes to a much higher extent. Additionally, neutral compounds with a high degree of covalent binding can be formed in the presence of halides. During preliminary studies it became obvious that also negatively charged complexes of mercury are exchanged at the clay. During repetitive measurements the signal heights increased steadily although after regeneration of the electrode surface no re-oxidation signal could be observed. The reproducibility of the results was therefore very poor and the method could not be applied to analytical purposes.

In the presence of high excess of NH₄⁺ salts and ammonia, mercury forms

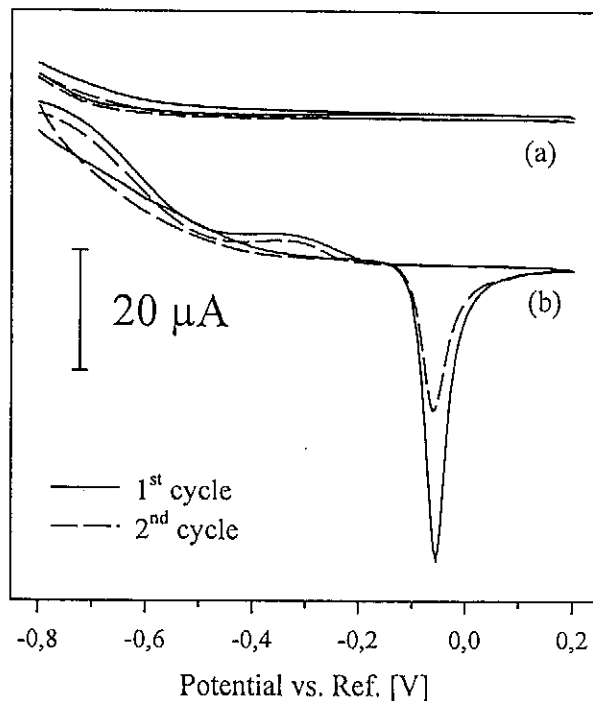


Fig. 11 Cyclic voltammograms of mercury(II) using a *montmorillonite*-modified carbon paste electrode: (I) blank; (II) 2.5 mg l^{-1} Hg(II) accumulated under open circuit conditions; supporting electrolyte: $0.1 \text{ M NH}_4\text{SCN}$, 0.01 M HClO_4 ; accumulation time 120 s ; scan rate 20 mV s^{-1}

a very stable amine complex $[\text{Hg}(\text{NH}_3)_4]^{2+}$ [10]. Mercury was therefore preconcentrated from an ammonia/ammonium nitrate buffer. The optimum pH for preconcentration is 8.2 to 8.5, corresponding to 0.01 M NH_3 and $0.05 \text{ M NH}_4\text{NO}_3$.

The graphs showing the dependence of the voltammetric signal on the preconcentration time are rather similar to that of copper except that the quasi-linear range is somewhat shorter, which is explainable by the different accumulation medium used.

Calibration curves of mercury were established by applying suitable preconcentration periods (Fig. 13). Small concentrations of Hg^{2+} in combination with short preconcentration times show a slight exponentially increasing dependence of the current response on the concentration of the analyte (curve a). Migrational effects may be the reason for this, since the tetramine complex is rather voluminous and has therefore a smaller mobility than the free ion. Determinations of mercury applying the internal standard addition method are therefore not possible with preconcentration times less than five minutes. The calibration curves show linear dependence of the DPV current in a concentration

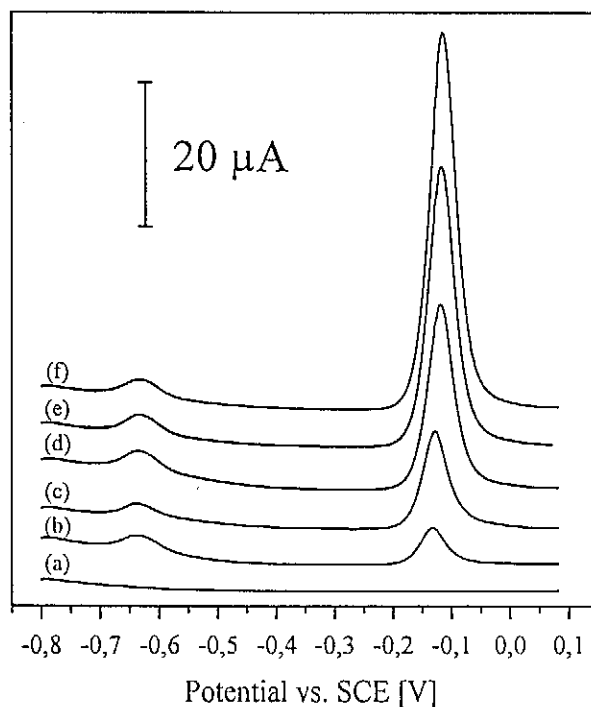


Fig. 12 Differential pulse voltammograms of mercury(II) using a *montmorillonite*-modified carbon paste electrode: supporting electrolyte: 0.1M NH_4SCN , 0.01 M HClO_4 ; accumulation time: 120 s; scan rate 10 mV s^{-1} ; analyte solutions: 0.05 M NH_4NO_3 , 0.01M NH_3 ; (a) blank, (b) $200 \mu\text{g l}^{-1}$ Hg(II), (c) $400 \mu\text{g l}^{-1}$ Hg(II), (d) $600 \mu\text{g l}^{-1}$ Hg(II), (e) $800 \mu\text{g l}^{-1}$ Hg(II), (f) $1000 \mu\text{g l}^{-1}$ Hg(II)

range from 50 to $600 \mu\text{g l}^{-1}$ Hg(II) (curves (b) and (c)). The relative standard deviation is 6.2 % for 5 repetitive measurements after accumulation of $100 \mu\text{g l}^{-1}$ Hg(II) for 300 s. The detection limit (3σ -value) is $10.2 \mu\text{g l}^{-1}$ for a preconcentration time of 10 minutes.

The effect of interferences on the determination of mercury(II) is reflected in Table V. The presence of silver ions in the analyte solution results in a broad overlapping signal around 0 V vs. SCE. Silver ions also form a positively charged diamine-complex $[\text{Ag}(\text{NH}_3)_2]^+$ and are exchanged into the clay. As expected also Hg(I) interferes severely since it is accumulated in the clay and cannot be discriminated from Hg(II) after its reduction to the elemental state.

Copper(II) in higher concentrations interferes the mercury response due to amalgamation and overlapping signal. Chloride has no notable influence on the current response of mercury.

The method was applied for the determination of mercury in water from the river Mur sampled in the area of Graz. The sample was spiked with $100 \mu\text{g l}^{-1}$ Hg(II). The filtered sample was pretreated with HNO_3 and UV radi-

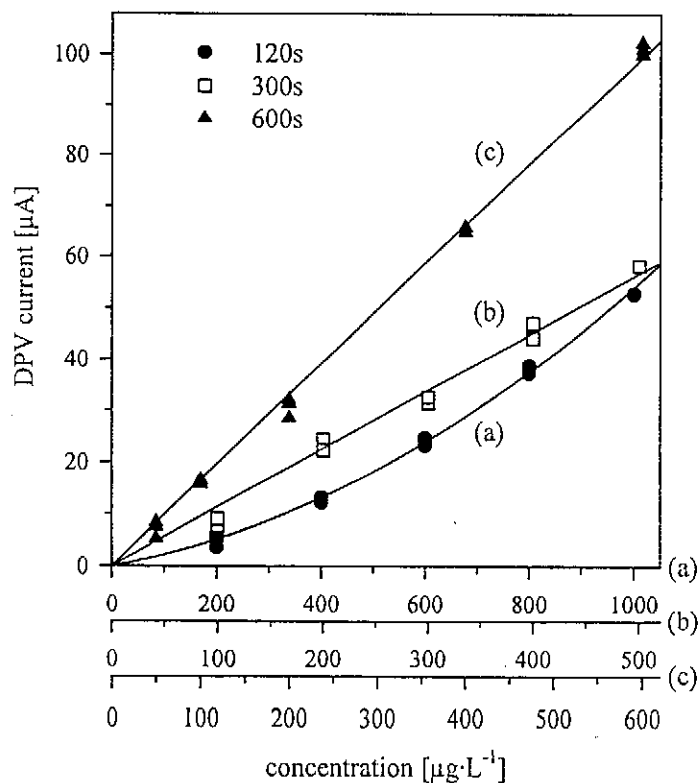


Fig. 13 Dependence of the DPV peak current on the concentration of mercury(II) in the analyte solution: supporting electrolyte: 0.1 M NH_4SCN , 0.01 M HClO_4 ; analyte solution: 0.05 M NH_4NO_3 , 0.01 M NH_3 ; accumulation time: (a) 120 s, (b) 300 s, (c) 600 s

tion for 6 hours. Applying a preconcentration time of 10 minutes the Hg^{2+} concentration in the sample was found to be $95.3 \pm 4.7 \mu\text{g l}^{-1}$. Although the recovery rate of 95.3% can be regarded to be sufficient for this concentration, the method for the voltammetric determination of mercury(II) using a montmorillonite- modified carbon paste electrode seems to be poorly applicable to environmental samples since the practical detection limit is rather high.

Model to Describe Preconcentration of Divalent Cations under Open Circuit Conditions

Kalcher et al. published a paper dealing with the evaluation of a model to describe preconcentration of mono- and divalent cations at a *vermiculite*-modified carbon paste electrode [1]. Like *montmorillonite*, *vermiculite* is a clay mineral with distinctive ion exchange properties and therefore the preconcentra-

Table V Change of DPV peak current caused by interfering species: supporting electrolyte: 0.1M NH₄SCN, 0.01M HClO₄; analyte solution: 0.05M NH₄NO₃, 0.01 M NH₃; 250 µg l⁻¹ Hg(II); accumulation time 120 s

Interferent	Added as	Change of peak current [±%]	
		Concentration of interferent	
		500 µg l ⁻¹	5000 µg l ⁻¹
Cu ²⁺	CuSO ₄ /H ₂ O	-85.1	-100
Ag ⁺	AgNO ₃ /0.5 M HNO ₃	+394	+3200
Fe ³⁺	FeCl ₃ /6 M HCl	+16.3	-66.3
Hg(I)	Hg ₂ Cl ₂ /H ₂ O	+404	+3200
Pb ²⁺	Pb(NO ₃) ₂ /0.1 M HNO ₃	-52.7	-69.3

Interferent	Added as	Change of peak current [±%]	
		Concentration of interferent	
		1 mg l ⁻¹	10 mg l ⁻¹
Cl ⁻	NaCl/H ₂ O	-4.3	-10.1

tion is based predominantly on ion exchange. Starting from the law of mass actions and expressing activities in terms of voltammetric currents, the authors established a model by which preconcentration of copper and silver could be described very well.

One parameter obtained by the model is the conditional equilibrium constant K''_{eq} of the ion exchange reaction (Eq. (6)). This parameter has a direct meaning only for the electrochemical experiment itself, but can be usefully exploited for comparisons with results from other systems.

$$K''_{eq} = \frac{1}{4f_{I \rightarrow C}} \cdot \frac{1}{[A^{2+}]_{(sol)}} \cdot \frac{I_{cq}}{(I_{max} - I_{cq})^2} \quad (6)$$

Kalcher et al. also established a model to describe the kinetics of the accumulation process under open circuit conditions. The results of this kinetic model are the rate constant K_v and the current under equilibrium conditions I_{eq} with respect to a definite concentration of the analyte in the bulk solution (Eq. (7)), which must be known to estimate the equilibrium constant K''_{eq} . To calculate the parameters derived from the model, coulometric measurements are indispensable in order to obtain the conversion factor $f_{I \rightarrow C}$.

$$I_t = I_{eq} \cdot \left(1 - \frac{1}{4f_{I \rightarrow C} k_v I_{eq} [A^{2+}]_{(sol)} t + 1} \right) \quad (7)$$

The most valuable parameter derived from the model is the thickness of the *mean reaction layer* ϑ , which is hardly available by other models. It can be estimated by equalling the maximum preconcentratable amount of the analyte at the modified electrode surface and the ion exchange capacity of the modifier (Eq. (8)). The ion exchange capacity can be determined by batch experiments.

$$\vartheta \geq \frac{1}{\rho m_M} \cdot \frac{[A^+]_{(max,surf)}}{[A^+]_{(max)}} \quad (8)$$

- ρ specific mass of the paste, kg m^{-3}
 m_M mass ratio of the clay in the paste
 ϑ thickness of the mean reaction layer, m
 $[A^+]_{(max,surf)}$ maximum preconcentratable amount of the analyte at the modified electrode surface
 $[A^+]_{(max)}$ ion exchange capacity of the modifier

According to the model for the accumulation of divalent cations described by Kalcher et al., investigations dealing with the preconcentration of the heavy metals under investigation were performed. To model preconcentration under open circuit conditions, the following experiments were performed:

- Dependence of the currents on the preconcentration time for several concentrations of the analytes.
- Determination of the ion exchange capacity of *montmorillonite* by means of batch experiments with respect to the different analytes.
- Determination of the conversion factor $f_{I \rightarrow C}$ by means of coulometric experiments.

The model describing the kinetics of the accumulation process allows estimation of the currents when equilibrium conditions are already reached. From these data the equilibrium constant of the ion exchange reaction at the modified electrode surface can be estimated. The model is well applicable to describe the dependence of the amount of electroactive species at the electrode surface on the preconcentration time as shown in Fig. 14 in the case of lead(II).

Figure 15 displays the dependence of I_{eq} on the bulk concentration of lead as predicted by the model compared with data calculated from kinetic studies. The congruence is excellent so that it may be assumed that the model describes the experimental conditions quite well.

The equilibrium constant for the ion exchange reaction of the analytes

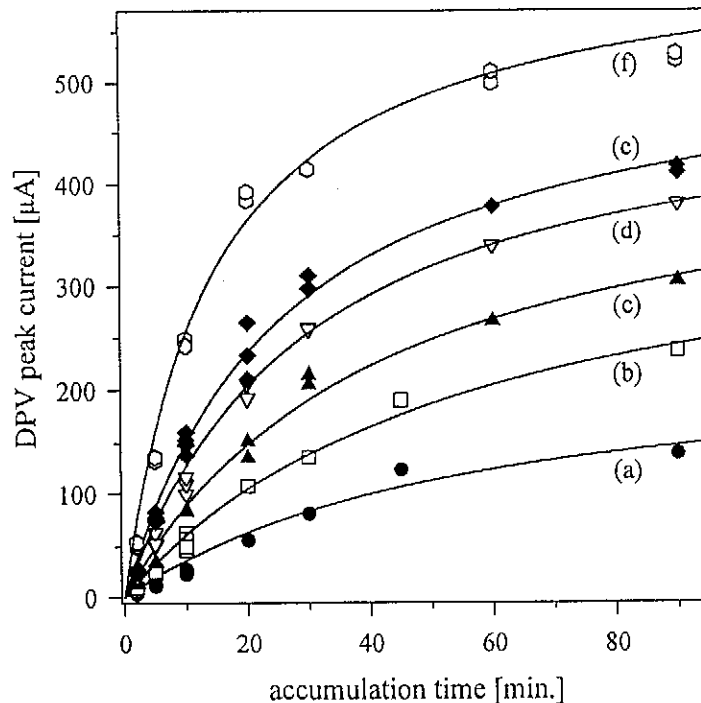


Fig. 14 Dependence of the lead(II) DPV signal current on the preconcentration time: supporting electrolyte: 0.1 M KCl, 10^{-3} M HCl; analyte solutions: 2.5×10^{-4} M HNO_3 , (a) $25 \mu\text{g l}^{-1}$ Pb(II), (b) $50 \mu\text{g l}^{-1}$ Pb(II), (c) $75 \mu\text{g l}^{-1}$ Pb(II), (d) $100 \mu\text{g l}^{-1}$ Pb(II), (e) $150 \mu\text{g l}^{-1}$ Pb(II), (f) $250 \mu\text{g l}^{-1}$ Pb(II); solid lines are calculated by the model

under investigation with *montmorillonite* suspended in solution was determined by batch experiments with AAS and ICP-MS. The results are shown in Fig. 16 for lead(II) as analyte; the fitted curves show excellent congruence with the experimental results.

For all four divalent cations investigated the congruence between experimental and modelled values was very good. Therefore it can be stated that with this model the accumulation of divalent cations under open circuit conditions can be described.

The experimental and model parameters for the investigated metals and for the reported preconcentration of copper(II) with *vermiculite* [1] are summarized in Table VI.

An overall comparison shows that with *montmorillonite* the *mean reaction layer* varies from 2 to $4.5 \mu\text{m}$, which is somewhat thicker than with *vermiculite* ($0.7 \mu\text{m}$). The reason can be the different chemical nature of the modifiers as well as the different pre-treatment procedures. The electrochemical equilibrium constants K'_{eq} range between 7×10^9 and $2 \times 10^{10} \text{ l m}^{-2} \text{ mol}^{-2}$ and are in average

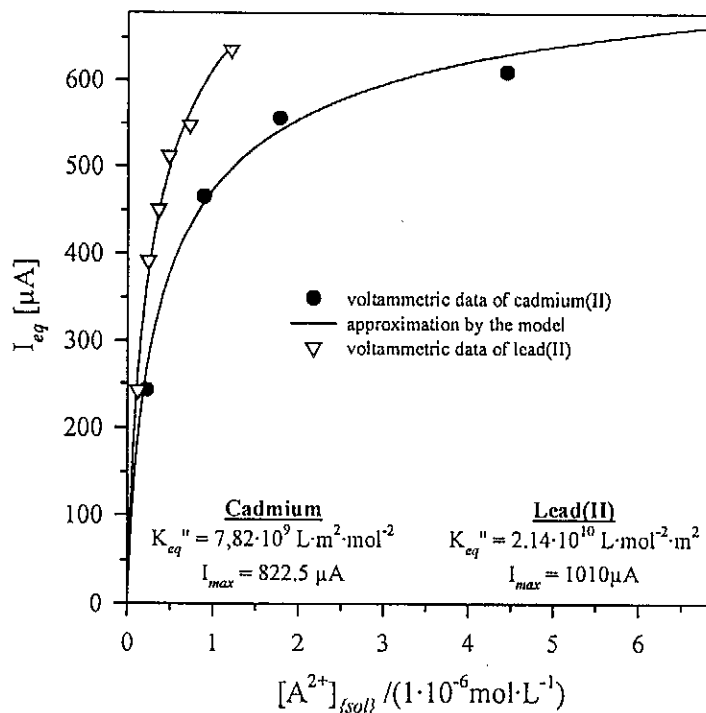


Fig. 15 Dependence of the DPV peak currents at equilibrium conditions on the concentration of cadmium(II) and lead(II) in the analyte solution: cadmium: supporting electrolyte 0.075 M NH_4Cl ; lead: supporting electrolyte: 0.1 M KCl , 10^{-3} M HCl

one order of magnitude higher than those for the system copper - *vermiculite*. This trend is also reflected in K_{eq}'' obtained from batch experiments.

A comparison between K_{eq}'' derived from electrochemical experiments and K_{eq} from batch experiments shows an almost excellent correlation (Fig. (17)).

Thus, the simplified model describing the preconcentration of divalent cations can be used very well to predict kinetic and conditional parameters. It can also be applied to estimate equilibrium constants from electrochemical experiments by comparison of different analytes, when at least the conditional K_{eq} of the ion exchange reaction between one species and the modifier is known.

The model could also be a very valuable tool for estimating the *mean reaction layers* of the surface involved into the accumulation process, a parameter which is hardly accessible by other means. With restrictions it can even be used to estimate chemically varying systems as long as border limits (modifier concentration, preconcentration reaction) are considered.

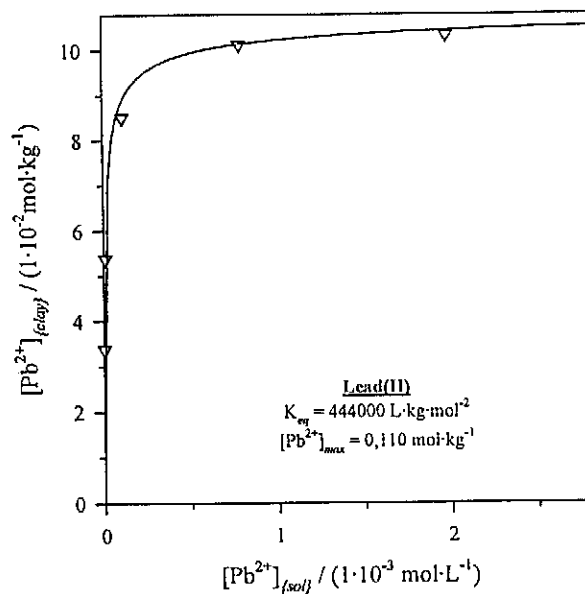


Fig. 16 Equilibrium concentrations of lead(II) in *montmorillonite* and in solution as determined by FAAS measurements (batch experiments)

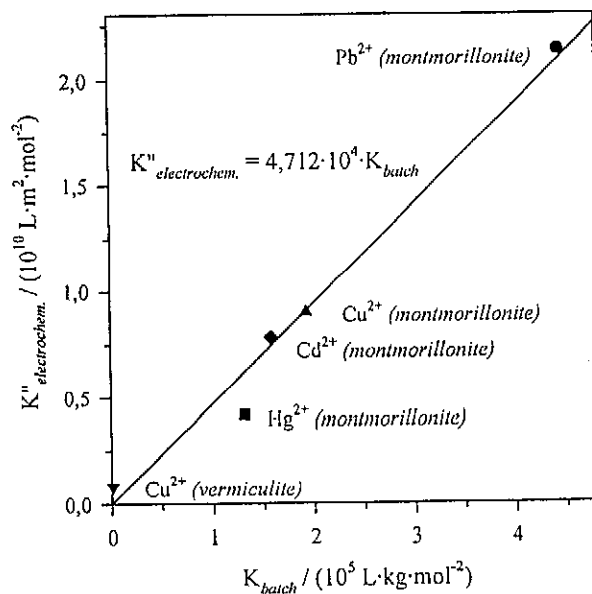


Fig. 17 Correlation between equilibrium constants derived from electrochemical experiments (calculated from the model) and equilibrium constants obtained from batch experiments

Table VI Model and experimental parameters of cadmium, lead, copper and mercury accumulated at *montmorillonite* and of copper accumulated at *vermiculite* [1]

Parameter	Copper	Mercury	Cadmium	Lead	Copper (vermiculite)
K_{eq}^n , $l\ m^{-2}\ mol^{-2}$	9.00×10^9	4.22×10^9	7.82×10^9	2.143×10^9	8.26×10^8
I_{max} , μA	580	476	822.5	1010	180.8
K_v , $l\ m^{-2}\ mol^{-2}$	4.72×10^7	2.58×10^8	6.74×10^7	7.302×10^8	2.40×10^7
K_{eq} , $l\ kg\ mol^{-2}\ s^{-1}$	1.982×10^5	1.312×10^5	1.579×10^5	4.440×10^5	1.168×10^3
$[A^{2+}]_{(max)}$, $mol\ kg^{-1}$	1.10×10^{-1}	3.5×10^{-2}	1.120×10^{-1}	1.10×10^{-1}	2.80×10^{-1}
$f_{I \rightarrow Q}$, $\mu C\ \mu A^{-1}$	1.291	1.132	1.517	5.516×10^{-1}	2.386
$f_{I \rightarrow C}$, $mol\ m^{-2}\ \mu A^{-1}$	1.052×10^{-7}	9.220×10^{-8}	1.236×10^{-7}	4.493×10^{-8}	1.974×10^{-7}
$[A^{2+}]_{(max, surf)}$, $mol\ m^{-2}$	6.102×10^{-5}	4.389×10^{-5}	1.017×10^{-4}	4.538×10^{-5}	3.51×10^{-5}
δ , m	$\geq 2.75 \times 10^{-6}$	$\geq 6.21 \times 10^{-6}$	$\geq 4.49 \times 10^{-6}$	$\geq 2.02 \times 10^{-6}$	$\geq 7.2 \times 10^{-7}$

Conclusion

In the work presented here a carbon paste electrode modified with the clay mineral *montmorillonite* was used to develop a method for the voltammetric determination of cadmium(II), lead(II), copper(II) and mercury (II). The analytical method is based on the ion exchange properties of *montmorillonite* and, consequently, on the preconcentration of the electroactive species at the modified electrode surface. Compared with other electroanalytical methods using clay-modified electrodes, the pre-treatment of *montmorillonite* during the swelling step leads to an improved behaviour of the clay as far as the ion exchange properties and the mechanical and electroanalytical characteristics (e.g. mechanical stability, background currents) of the modified carbon paste electrode surface are concerned.

Another aim of the work presented here was to model preconcentration of divalent cations under open circuit conditions. The model described by Kalcher et al. was designed for the description of the accumulation of mono- and divalent cations [1]. The results obtained for the metals under investigation underline the applicability of the model to describing preconcentration of

divalent cations under open circuit conditions. Experimental data and approximations calculated from the model are in very good accordance. Especially the linear correlation between equilibrium constants obtained from batch experiments and those obtained from electrochemical measurements underlines the descriptive applicability of the model.

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