

Alain Walcarius · Jérôme Devoy · Jacques Bessiere

Silica-modified electrode for the selective detection of mercury

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Abstract Pure silica particles were dispersed within carbon paste and the resulting modified electrode was applied to the selective voltammetric detection of mercury(II) species after their accumulation at open circuit. The remarkable selectivity observed between pH 4 and 7 was attributed to the intrinsic adsorption mechanism which involves a condensation reaction between mercury(II) hydroxide and hydroxyl groups on the silica surface, leading to the formation of an inner-sphere-type surface complex. After optimization with respect to the electrode composition, the detection medium, and the voltammetric scan mode, a linear response was obtained in the concentration range between 2×10^{-7} M to 1×10^{-5} M, by applying anodic stripping square wave voltammetry. Various silica samples were used and their sorption behavior was discussed in relation to their specific surface area and porosity. The effect of chloride and pH on the accumulation of mercury(II) on silica was also investigated.

Key words Electroanalysis · Silica · Modified electrodes · Preconcentration · Voltammetry

Introduction

The chemical modification of conventional electrodes with a suitable reagent is becoming an extensively developed approach for controlling the rates and selec-

tivities of charge transfer reactions at solid/liquid interfaces. Chemically modified electrodes [1] are currently involved in many research areas, such as electroanalysis, electrocatalysis, membrane barriers, electroreleasing, micro- and nanostructures, and biosensors. In the last decade, silicate-based materials such as clays [2–5], zeolites [4–10], or silicas and some other metal oxide minerals [11–14] were used in connection with electrochemistry, where their remarkable and sometimes unique properties have been exploited. Electrodes modified with these solids have found applications in chemical sensing and as biosensors [3, 9, 10, 13, 14]. For example, silica-modified electrodes may exploit a chemical reaction in open circuit for the accumulation of a selected species prior to its voltammetric quantification, leading to appreciable improvements in either sensitivity or selectivity with respect to conventional indicating electrodes [15–19]. On the other hand, their huge success in bioelectrochemistry is related to the ability of silicates to encapsulate biologicals without preventing their activity [20–22]. Contrarily to electrodes designed from organically modified silicates, the use of pure silica-modified electrodes for the amperometric detection of a target analyte, after its adsorption on the silica surface, remains uncommon [18, 19, 23–25]. We have previously described the use of a carbon paste electrode modified with silica gel for the preconcentration of copper(II) from an aqueous ammoniacal medium and its subsequent voltammetric detection in acidic solutions [18, 19]. The accumulation involved the ionization of the silica surface (transformation of silanol into silanolate groups) prior to the binding of $\text{Cu}(\text{NH}_3)_4^{2+}$ cations [18]. Though rather selective, the sensor failed at high ionic strength because a high concentration of cations resulted in competition for the ion exchanging sites [19], as is common for electrochemical sensors based on ion exchangers [26]. Since mercury(II) can be adsorbed on silica without requiring the formation of silanolate groups [27], a silica-modified electrode could exhibit improved selectivity for the detection of this species

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A. Walcarius (✉) · Jérôme Devoy · Jacques Bessiere
Laboratoire de Chimie Physique pour l'Environnement,
Unité Mixte de Recherche UMR 7564,
CNRS – Université H. Poincaré Nancy I,
405 Rue de Vandoeuvre,
54600 Villers-les-Nancy, France
e-mail: walcariu@lcpce.cnrs-nancy.fr
Tel.: +33-383-916343; Fax: +33-383-275444

with respect to other metal cations. Various electroanalytical methods have been applied to the determination of mercury, and significant improvements in both sensitivity and selectivity were gained by using chemically modified electrodes [28–30]. The investigation of highly selective modifiers might lead to further progress in this field.

In this paper, we assess the benefit of the incorporation of silica gel within carbon paste for improving the selectivity of the accumulation of mercury(II) at the electrode surface prior to its voltammetric detection in acidic medium. Special attention will be given to the adsorption mechanism, the effect of pH, and the influence of the presence of chloride species in the preconcentration medium.

Experimental

Voltammetry experiments were performed using a Model 283 potentiostat/galvanostat monitored by M270 electrochemical research software (EG&G Princeton Applied Research), and equipped with a three-electrode system mounted on a 50-ml cell. The counter electrode was a platinum wire and a calomel electrode (Metrohm, no. 6.0724.100) served as reference. The working electrodes were home-made silica-modified carbon paste electrodes (SMCPEs). They were prepared by mixing weighed amounts of silica (Kieselgel 60, Merck), high purity graphite (Ultra F, <325 mesh, Alfa), and mineral oil (Aldrich) thoroughly until uniformly wetted paste was obtained. Portions of the resulting composite material were then packed into the end of a home-made PTFE cylindrical tube equipped with a screwing stainless steel piston. The surface was smoothed on a piece of weighing paper.

Most experiments were performed using the chromatographic grade silica gel "Kieselgel 60" (Merck), characterized by a specific surface area of $425 \pm 25 \text{ m}^2 \text{ g}^{-1}$ (determined by N_2 adsorption: BET method) and a hydroxyl concentration of $3.8 \pm 0.2 \text{ mmol OH g}^{-1}$ [31]. Other pure silica materials were used for comparison purposes. The pyrogenic silica Aerosil-200 (Degussa) contained about $1.4 \text{ mmol OH g}^{-1}$, for a specific surface area of $200 \text{ m}^2 \text{ g}^{-1}$ (BET N_2). Microporous monodisperse silica beads, obtained according to the Stöber procedure [32], displayed a pore aperture of 3 \AA with an internal silanol population of about $5.2 \text{ mmol OH g}^{-1}$ [31]. The pure silica MCM-41 sample was a high specific area [ca. $1050 \text{ m}^2 \text{ g}^{-1}$ (BET N_2)] mesoporous (pore aperture: 2.9 nm) silica containing an estimated hydroxyl concentration of 8 mmol OH g^{-1} [33].

All chemicals were analytical grade. All solutions were prepared with high purity water (resistivity: $18 \text{ M}\Omega \text{ cm}$) obtained from a Millipore Milli-Q water purification system. The certified standard solution of mercury(II), at $1.001 \pm 0.002 \text{ g l}^{-1}$, was from Merck. Mercury solutions were prepared daily by diluting a stock solution of $1.00 \times 10^{-4} \text{ M}$ mercury nitrate (Merck) in high purity water. Adjustment of pH was made by addition of either HNO_3 or NaOH ; no buffer was used to avoid any eventual complexation of mercury by one of the buffer components.

The general procedure for mercury(II) detection includes a preconcentration step achieved from stirred solutions containing the target analyte at a given concentration and selected pH, followed by medium exchange of the electrode into the separate voltammetric cell containing the acidic supporting electrolyte (0.1 M HNO_3), where voltammetric monitoring was performed in the anodic stripping square wave mode. Typically, a potential of -0.5 V was held during 30 s under quiescent conditions and square wave voltammograms were recorded with a 100 Hz frequency, a 5 mV step height, and a 50 mV modulation amplitude. No regeneration of the electrode surface was required providing complete

leaching of the previously accumulated mercury was ensured during the detection step.

Results and discussion

Voltammetric detection of mercury(II) after accumulation at the SMCPE

Figure 1 shows representative anodic stripping square wave voltammograms recorded in acidic medium (0.1 M HNO_3) after accumulation at open circuit during selected periods of time from a $5 \times 10^{-6} \text{ M}$ mercury(II) solution at pH 5. They display a well-defined anodic peak located at $+0.2 \text{ V}$, corresponding to the oxidation of metallic mercury(0) formed during electrolysis of the previously accumulated mercury(II) species. The intensity of peak currents increased linearly with increase in the time afforded to the electrode to stay in the accumulation cell, where accumulation of mercury(II) at the electrode surface was occurring. At the same time, no peak was observed when using an unmodified carbon paste electrode, indicating that adsorption of mercury(II) on the silica surface is responsible for the preconcentration process. Square wave voltammetry was preferred compared to linear scan, or to a less extent to differential pulse, voltammetry for its better sensitivity.

The quantitative determination of the accumulated mercury(II) species implies their complete electrolysis before the anodic stripping. It was therefore checked how much time was required to desorb all the previously accumulated species and to ensure their concomitant reduction during the electrolysis step. For mercury concentrations lower than $1 \times 10^{-5} \text{ M}$ and preconcentration duration less than 5 min , it was observed that 30 s were enough to obtain quantitative results; a longer time did not result in more intense voltammetric signals while shorter times led to lower peak currents. Of

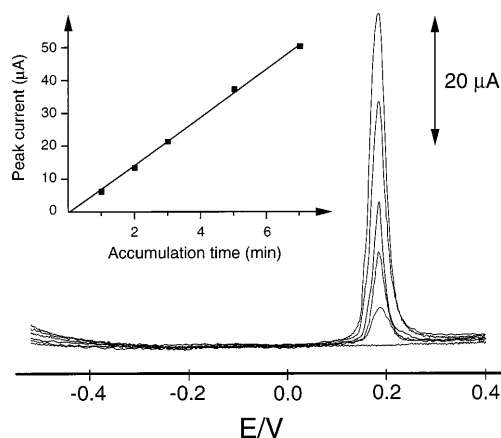


Fig. 1 Anodic stripping square wave voltammograms recorded at a SMCPE in 0.1 M HNO_3 after accumulation during selected periods of time at open circuit from a $5.0 \times 10^{-6} \text{ M}$ mercury solution (pH 5), and 30 s electrolysis at -0.5 V . Inset: anodic peak currents as a function of preconcentration time

particular note in this easy and fast desorption behavior is the fact that regeneration of the electrode surface was entirely achieved during the detection step, therefore avoiding any additional regeneration step which is often a major problem, limiting full realization of improvements brought by modified electrodes for practical field applications (although carbon paste electrode surfaces can be renewed by simple mechanical smoothing [34], this advantage is only valid for pastes of homogeneous composition, which is not easily obtained with solid particulate modifiers). In such conditions, more than 30 successive measurements were performed for the analysis of 5×10^{-6} M mercury(II) without any deterioration of the voltammetric signal (relative SD: 1.5%, $n = 10$). This makes the technique suited to routine analysis, very simple, and consequently user-friendly for non-specialists.

The composition of the SMCPE was found to affect the voltammetric response. As shown in Fig. 2A, the mineral oil content has a dramatic influence, considering that the optimum percentage of this organic binder into the paste is distributed in a narrow range (between 28% and 31%). Oil contents lower than 25% or higher than 35% did not give significant signals. Limitations at high percentages are probably due to higher hydrophobicity of the electrode surface, somewhat preventing its dissolution by the solution, while the harmful effect observed at low loadings is not understood. A possible explanation could be the low mechanical stability of the paste

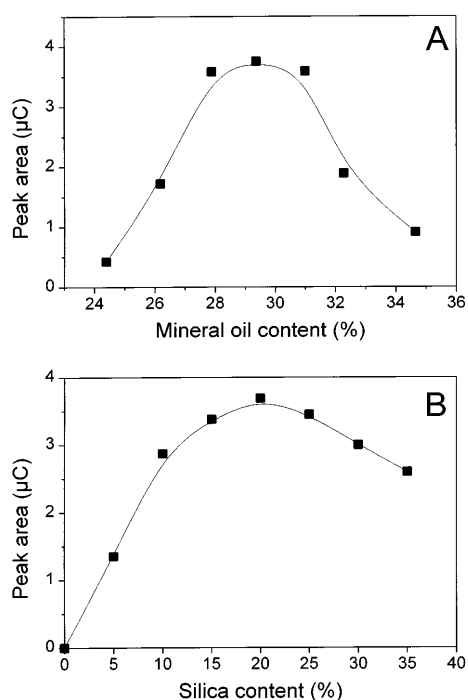


Fig. 2 Dependence of the voltammetric response (expressed as the anodic stripping peak area) obtained using a SMCPE on **A** the mineral oil content and **B** the silica content in the paste. Accumulation: 2 min from a 1×10^{-5} M mercury solution (pH 5.5); detection: square wave voltammetry after 1 min electrolysis at -0.5 V

upon decreasing the oil content, resulting in the leaching of silica particles into the solution. The silica content in the paste also has a profound effect upon the sensitivity of the SMCPE (Fig. 2B). The electrode response was rapidly raised when increasing the silica content up to 10%, then tended to level off, and even decreased for contents higher than 20%. The rapid increase is easily explained by larger amounts of adsorption sites for mercury at the electrode surface, and the slow decrease can be rationalized by considering the smaller effective surface area of the electrode (and lower conductivity) upon increasing the silica content.

After optimization with respect to the electrode composition, pH (see below), time of accumulation, potential and time of deposition, and stripping potential waveform, a linear dependence of peak areas (charge) was observed in the range of 2×10^{-7} M to 1×10^{-5} M mercury(II), with a detection limit of about 5×10^{-8} M (as estimated from a signal-to-noise ratio of 3). These results were obtained after 10 min accumulation from mercury solutions at pH 5.5, applying an electrolysis at -0.5 V during 1 min followed by an anodic stripping voltammetry in the square wave mode in 0.1 M HNO_3 (optimal conditions).

Adsorption mechanism and selectivity

As expected for adsorption of metal species on silica [35], the interactions of mercury(II) with the silica surface are strongly influenced by the solution conditions. This can be monitored by voltammetry at the SMCPE, as shown in Fig. 3. Adsorption was negligible at pH values lower than 2, then increased rapidly from 2 to 4, and reaching a maximum constant value up to pH 8. The shape of this isotherm may be explained by considering the speciation of both mercury(II) in solution and the surface state of silica as a function of pH (Fig. 4). At pH lower than 2, mercury(II) is essentially in the Hg^{2+} form which cannot react with the surface silanol groups of silica, especially because the silica surface is positive in this pH region [36]. On raising the pH,

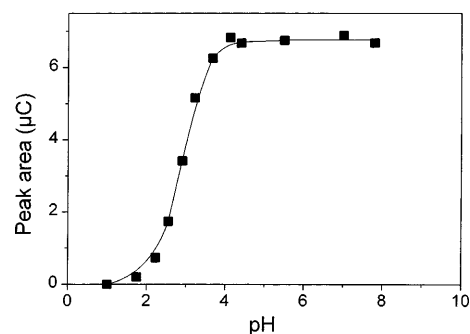


Fig. 3 Dependence of the voltammetric response of a SMCPE on the pH of the accumulation medium. Accumulation: 5 min from a 1×10^{-5} M mercury solution; detection: square wave voltammetry after 1 min electrolysis at -0.5 V

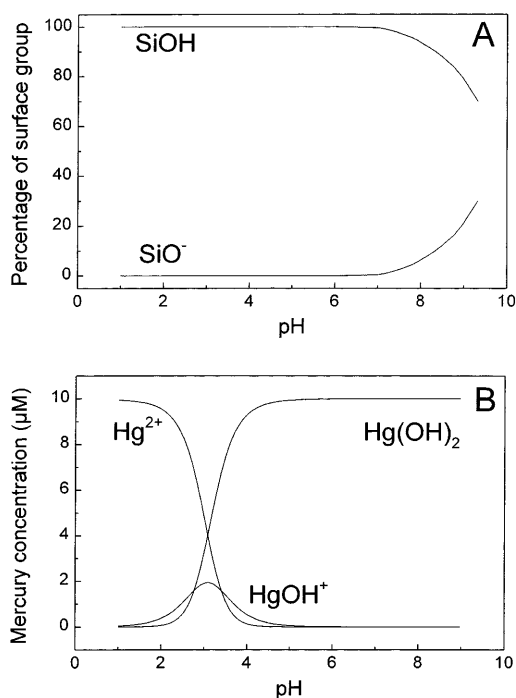
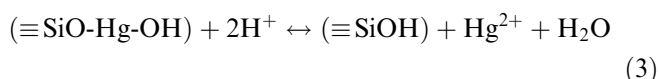
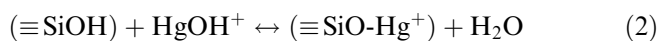
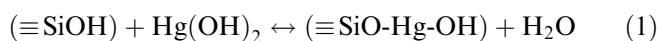


Fig. 4 Chemical form of the silica surface **A** and speciation of mercury (total concentration: 1.0×10^{-5} M) **B** as a function of pH

hydrolysis of mercury(II) occurs and $\text{Hg}(\text{OH})_2$ becomes rapidly the major species in the pH range between 3 and 9 (with some HgOH^+ around pH 3). At the same time, the majority of silanol groups located at the silica surface remains un-ionized, their deprotonation beginning slowly at pH values above 7. Adsorption is then explained by the reaction of $\text{Hg}(\text{OH})_2$ (and HgOH^+ to a less extent) with silanol groups (Eqs. 1 and 2), and desorption of the surface complexes can be achieved in a strongly acidic medium (Eq. 3). This adsorption mechanism [37, 38] is particular to mercury(II) which gives hydrolysis products soluble over the entire pH range (at concentrations lower than 2×10^{-4} M [39]), compared to that of most other metal ions which form less soluble metal hydroxides and lead to surface precipitation [40], auguring well for good selectivity of the SMCPE for mercury(II).



This illustrates why detection of mercury(II) at the SMCPE was only possible at pH values lower than 2; no response was obtained at pH values higher than 4 because no desorption occurred (pH values above 8 were not explored because of the low stability of silica in basic medium [35]).

The adsorption of mercury(II) onto the silica surface can be used as a selective preconcentration step prior to

the voltammetric measurement. The enhanced selectivity accrued from such an adsorption voltammetric experiment is indicated from the response for 1×10^{-5} M $\text{Hg}(\text{II})$ in the presence of alkali and alkaline earth metal cations or other transition metal species. The voltammetric measurements performed after transfer to the blank solution revealed that signals obtained for mercury after accumulation at pH 5 from a medium also containing Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Ca^{2+} , and Mg^{2+} , individually or in mixture and at concentrations up to 1 M, were essentially the same as that recorded for mercury alone (with recoveries varying from 97% to 102%). This constancy of the adsorption process with varying the ionic strength of the medium indicates the formation of an inner-sphere complex on the silica surface [41]. In addition, and more interestingly, the detection of mercury(II) was unaffected by the presence of many other metal species in the accumulation medium at pH 5, at the maximum concentration keeping soluble species at this pH or in more concentrated solutions providing only the soluble species reached the electrode surface. For example, 1×10^{-3} M of Cu^{II} , Co^{II} , Pb^{II} , Ni^{II} , and Zn^{II} at pH 5.5 led to a recovery of 99% for 1×10^{-5} M mercury(II). Such high selectivity is due to the particular adsorption mechanism for mercury on silica (Fig. 4, Eqs. 1 and 2), which essentially involves essentially the reaction of fully soluble hydrolyzed species at the silica surface. Between pH 4 and 7, the silica surface displays negligible ion exchange properties, preventing adsorption of metal cations (the vast majority of metal species in that pH range), otherwise the amount of soluble hydrolyzed metal species (other than those of mercury) is small enough not to interfere in the adsorption of mercury(II) hydroxide.

A special illustration of this high selectivity can be given for silver(I), which displays electrochemical behavior close to that of mercury(II). This was examined in solution phase experiments. Increasing amounts of silica particles were suspended in solutions containing either silver(I) or mercury(II) at pH 5.5, and the (eventual) depletion in the analyte concentration in solution was monitored by voltammetry at the rotating disk electrode. While the silver response remains upon the addition of silica over the entire content range, a significant decrease in the mercury response can be readily observed (Fig. 5), indicating depletion of the mercury concentration in the suspension because of its adsorption on the silica surface. No such collection is indicated in the presence of silver, demonstrating the ability of silica to discriminate between these two metal species. Once again, this is fully explained by considering data of Fig. 4 and the speciation of silver in solution. At pH 5, silver is essentially in the Ag^+ form, which cannot interact with the surface silanol groups. One can also notice from Fig. 5 that complete disappearance of solution-phase mercury was not observed, even for large silica loadings in the suspension, in agreement with similar experiments investigating mercury adsorption on goethite [42]. At pH 5.5, the

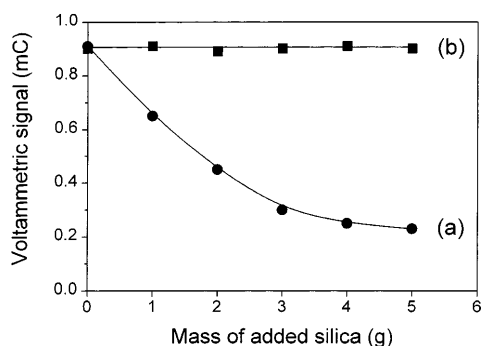


Fig. 5 Electrochemical monitoring of the solution-phase mercury (a) and silver (b) concentration upon the addition of silica powder into a 50-ml solution (initial concentration: 10^{-4} M). Results were obtained by differential pulse voltammetry at a glassy carbon electrode

adsorption of mercury(II) from a 1.0×10^{-6} M solution was not affected by the presence of 1.0×10^{-2} M silver(I).

Influence of the silica type

As various materials made of silicon oxide do exist, and as their surface properties can be very different depending on their nature and structure, this section aims to assess the effects of the silica type on the electroanalytical behavior of the SMCPE. Four silica-based materials were chosen for their very different intrinsic properties: Kieselgel 60 silica gel, pyrogenic silica Aerosil-200, mesoporous pure silica MCM-41, and monodisperse Stöber silica. Their main characteristics are listed in Table 1.

The voltammetric response of the SMCPEs made of these four silica-based materials was strongly affected by

Table 1 Characteristics of the silicates used for modification of the carbon paste, and the square wave voltammetric response of the corresponding SMCPEs

Materials	Specific surface area ^a ($\text{m}^2 \text{g}^{-1}$)	Average pore size (nm)	Silanol concentration ^b (mmol g^{-1})	Voltammetric signal ^c (μA)
Kieselgel 60	425	6	3.8	21
Aerosil-200	200	10	1.4 ^e	8
MCM-41	1050	2.9	8.0 ^f	10
Stöber silica	4 ^d	0.3	5.2	0.6

^a From BET N_2 adsorption experiments

^b By thermogravimetry, with respect to the dry silica mass

^c Currents sampled in stripping square wave voltammetry using the SMCPE, after 5 min accumulation at pH 4.5 in 10^{-5} M Hg(II) and 60 s electrolysis in 0.1 M HNO_3

^d This value is underestimated because N_2 is too large to probe the internal microstructure of Stöber beads [43]

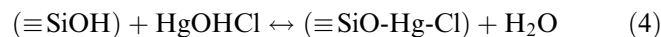
^e This value is underestimated because the surface of Aerosil-200 is covered by bonded siloxane groups which can be hydrolyzed in aqueous medium [44]

^f As determined from ^{29}Si NMR spectroscopy, after integration of the deconvoluted peaks assigned to $(\text{SiO})_3\text{SiOH}$ and $(\text{SiO})_4\text{Si}$ sites

the silica type (Table 1). Several factors are thought to intervene in the monitoring of mercury accumulation by adsorption on silica: the specific surface area and the silanol concentration (amount of adsorption sites), as well as the porosity of the materials (which define the number of accessible sites and limit the rate at which the analyte can reach these sites). Several cases can be distinguished from Table 1. When using large-pore silicas (Kieselgel 60, Aerosil-200), the efficiency of the accumulation step is controlled by the concentration of the binding sites (silanols). On decreasing the pore size of the adsorbent, however, the accumulation-detection processes become controlled by kinetic effects. Indeed, the voltammetric response observed using the mesoporous MCM-41 is half of that observed with silica gel, in spite of about a twofold binding capacity in the former case compared to silica gel. This result can be explained by the smaller pore aperture of MCM-41 compared to silica gel, which restricts diffusion of the analytes to the silanol in the adsorption step (and from these sites in the detection step), this limitation being not (enough?) counterbalanced by the very regular network of MCM-41 consisting of long and linear channels of constant critical dimensions [45]. The Stöber silica gave a very low electrochemical response because mercury hydroxide cannot fit inside the microporous structure, where most of the silanol groups were located.

Influence of chloride

Chloride is a well-known complexing ligand for mercury(II) and can compete with hydroxide, giving hydroxo and/or chloro complexes. Depending on the concentration of chloride, the most important species are $\text{Hg}(\text{OH})_2$, HgOHCl , and HgCl_2 (even HgCl_3^- and HgCl_4^{2-} in highly concentrated chloride solutions). It was shown earlier that HgCl_2 cannot adsorb on silica [27], because the Hg-Cl bond is so strong that reaction with SiOH is not possible. On the other hand, the existence of a mixed chloro-mercury surface complex ($\equiv\text{SiO-Hg-Cl}$) was demonstrated [42], confirming that adsorption of HgOHCl on the silica surface could take place according to a condensation reaction with silanol (Eq. 4), similar to the binding of $\text{Hg}(\text{OH})_2$ and HgOH^+ species.



The chloride concentration in the accumulation medium is then thought to affect the response of the SMCPE. This is shown in Fig. 6 for various pH values from 2 to 8. The general trend is a decrease in the sensitivity when increasing the chloride concentration, the evolution being sharper at lower pH values. This is explained by the adsorption mechanism indicating that only hydroxylated species of mercury(II), i.e. $\text{Hg}(\text{OH})_2$, HgOH^+ , and HgOHCl , are liable to adsorb on silica while others are rejected. As a consequence, the analysis of mercury(II)

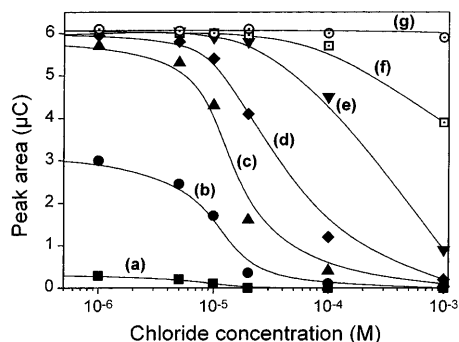


Fig. 6 Dependence of the voltammetric response of a SMCPE on chloride concentration in the accumulation medium, for various pH values: *a* 2, *b* 3, *c* 4, *d* 5, *e* 6, *f* 7, *g* 8). Other conditions as in Fig. 3

in the presence of chloride species, using the SMCPE, would require measurement at a pH high enough to maintain a high level of hydroxyl-containing mercury(II) species, or even after elimination of chloride by precipitation [i.e. with Pb(II)]. Alternatively, the electrochemical response of the SMCPE could be used for speciation studies since the electrode is sensitive to only the hydroxo and hydroxy-chloro complexes of mercury(II).

Conclusion

It can be stated that the use of pure silica as a modifier for a carbon paste electrode leads to the selective accumulation of mercury(II) species which can be subsequently detected by anodic stripping square wave voltammetry in acidic medium. Mercury binding to silica involves a condensation reaction between surface silanol groups and hydrolyzed mercury(II) species, so that this analyte is adsorbed on a material with a surface state displaying no significant ion exchange properties ($\text{pH} < 7$). The presence of chloride in the accumulation medium affects the SMCPE response by inducing a variation in the speciation of mercury. Finally, the use of various silica samples displaying different properties has demonstrated that diffusion of the analyte inside the porous structure is an important rate-determining factor, the high concentration of bonding sites on the silica surface not being the predominant factor giving high sensitivity. The proposed method could be applied in case of high-level mercury contamination (with respect to the rather poor detection limit) where high selectivity is required.

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