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Application of polymer-coated glassy carbon electrodes in anodic stripping voltammetry

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relative errors are summarized in Table II.

For monovalent cations, potassium shows the largest errors followed by ammonium and then lithium. It is well-known that divalent cations elicit minimal response in the steady-state mode with glass membranes of the type used here. This lack of response to divalent cations is thought to be a function of their slow mobilities within the glass membrane matrix (17). As shown in Table II, however, large transitory responses to divalent cations cause significant errors in the non-steady-state mode. The relative selectivity pattern is $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, which follows the pattern commonly associated with cation exchangers. These results suggest that the transient phenomenon is associated with an ion-exchange process with the hydrated region of the glass membrane. Such an ion-exchange process has been proposed in this regard (10, 12). For all cations, the magnitude of the inaccuracy is lower at higher sodium concentrations.

Results presented in this paper clearly demonstrate significant inaccuracies in the response of the sodium glass membrane electrode when operated in a non-steady-state mode. The time-dependent selectivity of the glass membrane, caused by rapid activity steps of cations, appears to be responsible for these inaccuracies. As a result, this electrode must be used with caution and optimal experimental conditions must be established for each particular application to minimize this time-dependent selectivity phenomenon. Several experimental parameters have been identified that can be used in such optimization studies. Even under optimal

conditions, however, the use of "effective" selectivity coefficients in the non-steady-state mode must be considered for glass membrane electrodes.

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Application of Polymer-Coated Glassy Carbon Electrodes in Anodic Stripping Voltammetry

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This paper describes the use of glassy carbon electrodes coated with Nafion perfluorosulfonate resin in anodic stripping voltammetry. The coating procedure, performed by applying a solution of the polymer to the electrode surface, is convenient and fast. Subsequently, mercury is plated onto the electrode. The thickness of the polymer film is so low that it does not impede mass transport of the analytes. In comparison with the conventional mercury film electrode, the main advantages of the modified electrode are improved resistance to interference from surface-active compounds, increased sensitivity when used in conjunction with differential voltammetric methods, and better mechanical stability of the mercury film. The analytical utility of the polymer-coated electrode is demonstrated by application to untreated urine samples.

One of the most common problems in anodic stripping voltammetry (ASV), when applied to the direct analysis of biological samples or polluted waters, is the interference effects caused by organic constituents of the sample matrix. Ad-

sorption of surface-active compounds onto the working electrode can interfere with the diffusional transport of the analyte and usually results in peak depression (1). Moreover, adsorption/desorption processes of organic compounds can yield tensammetric peaks which can interfere with or be mistaken for the metal peaks (2). Extraneous peaks can also be caused by redox processes of nonanalyte matrix constituents. Obviously, these interference effects greatly complicate the interpretation of stripping voltammograms, particularly in speciation analysis where sample pretreatment must be kept to a minimum.

Recently, coating of the working electrode with permselective membranes has been introduced as a means of circumventing the organic interferences in ASV. The function of the membrane is to prevent the organic interferents from reaching the interface at which the deposition/stripping process takes place. Obviously, a compromise between exclusion of organic matter and the unhindered transport of the metal ions must be sought. Stewart and Smart (3, 4) covered a glassy carbon electrode with a bulk dialysis membrane (1000 nominal molecular weight cutoff) through which a thin mercury film electrode was plated. For cadmium, excellent resistance toward organic interferences was obtained although the dialysis membrane to some extent interfered with the mass transport of the analyte. Owing to their thickness, bulk

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membranes suffer from the general drawback that the time required for equilibration with the contacting solution is of the same order of magnitude as the duration of a typical ASV experiment, and the response time of the electrode can become a limiting factor. Wang and Hutchins-Kumar (5) coated a thin mercury film electrode (TMFE) with a cellulose acetate membrane and also obtained good resistance toward organic interference. However, this electrode modification procedure requires at least 70 min, which is inconvenient for practical ASV work. In both approaches, the membrane becomes the limiting factor to mass transport of the analyte.

In this paper, we report on the characteristics of a Nafion-coated thin mercury film electrode (NCTMFE) for use in ASV. Nafion, a non-cross-linked perfluorosulfonate cation-exchange resin, has recently been used for electrode coating in a great variety of electrochemical studies, mostly in conjunction with immobilization of positively charged redox couples within the film coating (6, 7). The Nafion polymer is chemically inert, nonelectroactive, hydrophilic, and insoluble in water and thus possesses almost ideal properties for preparation of modified electrodes. The coating can be recast from a solution of the polymer which makes the electrode modification procedure convenient and fast. Moreover, ultrathin coatings can be prepared which pose minimum resistance to diffusion of the analyte and yet discriminate against organic species. Also, with very thin films, the "dead volume" within the polymer film is minimized which allows rapid electrode response to changed solution conditions (e.g., standard additions).

In this study, the practical utility of the NCTMFE has been assessed by application to trace metal analysis in untreated urine samples.

EXPERIMENTAL SECTION

Apparatus. Square-wave and differential pulse measurements were performed with a Metrohm 646 voltammetric processor, while a Princeton Applied Research Model 174 polarographic analyzer was used for linear sweep measurements. In all experiments, a laboratory-built electrochemical cell was used. The cell consisted of a 50-mL cylindrical Perspex beaker screwed into a Perspex cover in which were mounted the nitrogen delivery tube, a Metrohm 628-10 rotating glassy carbon electrode (3 mm diameter), a platinum coil counter electrode, and a Ag/AgCl (3 M KCl) reference electrode.

Reagents. All buffers and supporting electrolyte solutions were prepared from Merck Suprapur reagents and distilled water, while other chemicals were of analytical grade. The protein standard solution (Sigma) contained 0.5 g/L albumin and 0.3 g/L globulin. The sample of Nafion-125 obtained from E. I. du Pont de Nemours and Co. was dissolved in a 1/1 ethanol-water mixture according to the procedure previously described (8). The content of the Nafion in the resulting stock solution determined by evaporation of a small aliquot was found to be 0.21% (w/v).

Procedure. The glassy carbon working electrode was coated by applying a droplet of the Nafion solution to the electrode surface with a microliter pipet. In this study, three film thicknesses were investigated, prepared by applying (a) 2 μ L of a 1:1 dilution of the stock solution, (b) 2 μ L of the stock solution, and (c) 4 μ L of the stock solution. These coatings are referred to as low-, medium-, and high-thickness films, respectively. The solvent was allowed to evaporate, whereafter the formed film was dried with a hair-dryer for 60 s. As previously noted (9), this heat treatment step improves the stability and electrochemical performance of the Nafion-coated electrode. Mercury was deposited on the glassy carbon/Nafion substrate by adding 5×10^{-5} M mercury(II) nitrate to the supporting electrolyte medium and depositing at -800 mV vs. Ag/AgCl for 5 min. Mercury deposition was done in situ except in the analysis of urine samples in which preformed films were used.

Unless otherwise stated, a medium containing 0.07 M acetate buffer, pH 4.0 (prepared from sodium acetate and nitric acid), and 0.05 M NaCl was used in the electrochemical experiments. Solutions and samples were deaerated with nitrogen for 5 min

prior to ASV. Electrode rotation was stopped prior to recording of the stripping signal.

Urine samples were diluted 1/3 with water and analyzed by ASV shortly after sampling. For cadmium and lead determinations, the pH was adjusted to 5.5, while copper determination was carried out at pH 1.0. In both cases, pH adjustment was done with aliquots of concentrated hydrochloric acid.

The instrumental settings for square-wave anodic stripping voltammetry (SWASV) were as follows: modulation amplitude, 25 mV; modulation frequency, 125 Hz; effective scan rate, 30 mV/s. The instrumental settings used for differential pulse anodic stripping voltammetry (DPASV) were as follows: modulation amplitude, 50 mV; pulse repetition time, 1 s; effective scan rate, 6 mV/s. In the experiments with linear sweep anodic stripping voltammetry (LSASV), the scan rate was 50 mV/s.

RESULTS AND DISCUSSION

Microscopy Studies of Nafion Films. Visually, the Nafion coatings were transparent and appeared somewhat more dull than the bare glassy carbon electrode. Two zones were clearly discernible: a dull ring zone and a highly refractive center zone. The formation of the refractive pattern followed the gradual retraction of the evaporating Nafion solution during the preparation of the coating. The extent of the refractive zone decreased with high film thickness.

In an optical microscope (500 and 1000 \times magnification), the low- and medium-thickness Nafion films appeared smooth and uniform with very few macroscopic holes. With the high-thickness Nafion film, cracks in the coating extending down to the glassy carbon surface were observed. The cracks, the largest of which could be seen with the naked eye, developed during the evaporation of the Nafion solution and were mostly confined to the edge of the coating. However, these cracks were relatively few and well separated, and the fraction of the glassy carbon exposed by them was insignificantly small. Under the microscope, the general appearance of the coating was still uniform and smooth.

Plating of mercury onto the Nafion-coated electrodes changed the microscopic appearance dramatically, and a pattern of finely dispersed droplets was observed. From the photomicrographs it was not possible to determine whether the mercury was deposited below, within or on top of the Nafion film.

Mercury Deposition. Mercury electrodeposited onto the glassy carbon/Nafion substrate from mercury(II)-containing solutions could clearly be seen as a grayish deposit which first formed in the refractive center zone and gradually expanded toward the edge of the electrode with longer deposition times. The amount of mercury plated onto the NCTMFE was determined by performing the electrodeposition in a solution spiked with radioactive mercury-203 (total mercury, 2.2×10^{-5} M; 10-min deposition at -900 mV vs. Ag/AgCl). Subsequently, the electrode was rinsed and the mercury deposit dissolved in concentrated nitric acid. A low-thickness NCTMFE incorporated approximately half as much mercury as a bare glassy carbon electrode ($33\,300 \pm 2800$ counts/min for a bare electrode vs. $18\,100 \pm 1300$ counts/min for a Nafion-coated electrode ($n = 3$ for both measurements)). This result was quite surprising and encouraging, as a much higher depression of the mercury plating efficiency was expected in the presence of the polymer film. The amount of mercury deposited on the low-thickness NCTMFE was 3.2×10^{-9} mol, corresponding to an average thickness of 66 Å assuming uniform coverage of the electrode area. By comparison, the average thickness of the Nafion coating is approximately 2000 Å, assuming equal densities of the recast Nafion film and the bulk membrane (1.98 g/cm^3 (10)). In practice, however, the density of the recast polymer will be somewhat lower owing to water uptake during the radical dissolution procedure, and the calculated thickness should therefore be considered as a minimum value.

Table I. Effects of Nafion Coating on the ASV Peak Currents of Lead, Cadmium, and Copper

	$I_p(\text{Cd})/\mu\text{A}$			$I_p(\text{Pb})/\mu\text{A}$			$I_p(\text{Cu})/\mu\text{A}$		
	SW ^a	DP ^b	LS ^c	SW	DP	LS	SW	DP	LS
TMFE	0.6	3.5	1.1	1.5	6.2	1.4	5.2	1.3	0.9
low-thickness NCTMFE	5.2	9.7	1.2	8.2	11.0	1.3	1.8	2.0	0.9
medium-thickness NCTMFE	4.1	10.3	1.0	6.6	11.9	1.1	2.6	2.6	1.0
high-thickness NCTMFE	0.2	2.8	1.3	0.7	7.5	1.2	5.8	3.5	1.2

^{a-c} SW, DP, and LS are square wave, differential pulse, and linear sweep anodic stripping voltammetry, respectively. Experimental conditions were as follows: 2.0×10^{-7} M metal ion; preelectrolysis for 60 s at -900 mV vs. Ag/AgCl.

Hence, even for the low-thickness NCTMFE, the Nafion film is considerably thicker than the mercury layer. However, it cannot be concluded on the basis of the calculated nominal thicknesses that the mercury is fully contained within the polymer as the mercury may fill up the pores of the Nafion coating and extend beyond it.

Next, the question of the distribution of the mercury within the Nafion film was addressed. Although unusual charge propagation properties have been suggested for the Nafion polymers (11), it was believed that the reduction of the mercuric ions and the growth of the mercury phase took place at the glassy carbon/Nafion interface. This hypothesis was strongly supported by two observations. First, in a radiotracer experiment, a mercury-plated Nafion electrode was immersed in dimethyl sulfoxide (Me_2SO) which removed the Nafion quantitatively, leaving a clearly visible mercury deposit on the electrode. After removal of the remaining mercury with nitric acid, it was found that the mercury activity was distributed between the Me_2SO and the nitric acid in the ratio 3:7. The Me_2SO fraction is probably even overestimated because the rinsing water applied to the electrode after the film dissolution was pooled with the Me_2SO before the counting, and this water may have dislodged mercury droplets from the glassy carbon surface. It appears highly unlikely that the Nafion film could be dissolved without removing the bulk of the deposited mercury unless the mercury droplets are attached directly to the glassy carbon surface. Second, as discussed below, the NCTMFE showed considerably higher resistance toward interference from surface-active agents than the conventional TMFE, indicating that the polymer hinders the transport of the interferents to the mercury surface. Obviously, this protective mechanism can only be operative if the mercury is confined beneath or within the polymer film.

At the high-thickness NCTMFE, no visible mercury deposition was observed in the cracks which formed in the coating.

The Nafion coating stabilizes the formed mercury phase mechanically and prevents the coalescence or dislodgement of mercury droplets which may take place at the TMFE. In an experiment in which an eccentric and slightly vibrating rotating electrode was used, large areas of bare glassy carbon quickly developed at the normal TMFE, whereas no change in the visual appearance or performance of a NCTMFE was observed after prolonged use with the damaged rotator. Moreover, a NCTMFE withstands gentle wiping with filter paper, whereas this treatment completely ruins a TMFE. The improved mechanical stability of the NCTMFE is a major advantage if the analysis is carried out under strongly convective conditions or if the sample contains particulate matter.

ASV Response Characteristics of NCTMFE. As shown in Figure 1, the NCTMFE gives rise to well-defined SWASV signals for cadmium, lead, and copper. For comparison, the stripping signals were also recorded with DPASV and LSASV, and the peak currents obtained are given in Table I. Although repetitive preparations of the Nafion coating resulted in considerable variation in the ASV sensitivity of the electrode (see below), the data in Table I are qualitatively representative

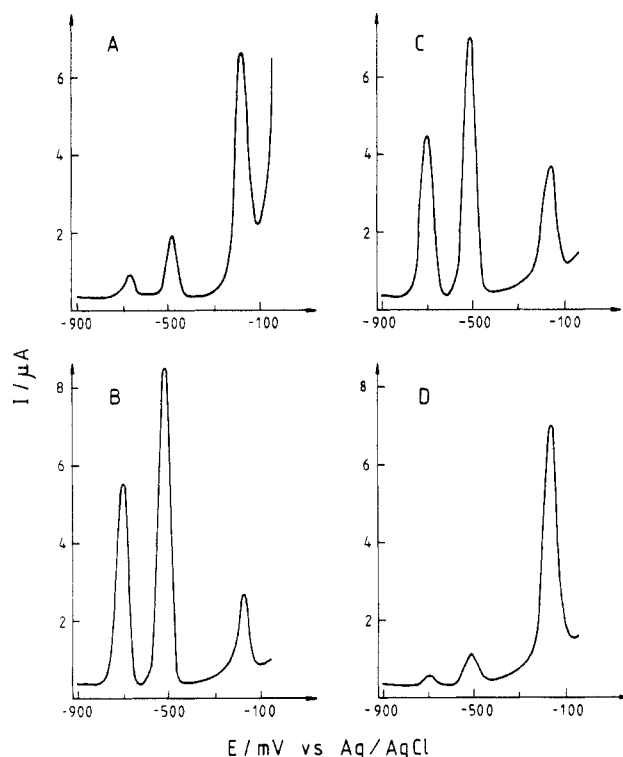


Figure 1. Square-wave stripping signals obtained with (A) TMFE and (B-D) low-, medium-, and high-thickness NCTMFE, respectively: 2×10^{-7} M cadmium, lead, and copper; preelectrolysis for 60 s at -900 mV vs. Ag/AgCl; electrode rotation rate, 500 rpm.

except that a high-thickness NCTMFE usually produced a lower copper signal than a medium-thickness NCTMFE. The unusual order of sensitivity for cadmium, lead, and copper obtained with SWASV at the uncoated TMFE, i.e., with the copper signal being much higher than those of the other two metals when present in equal molarity, differs from the order obtained with DPASV and requires a comment. It was found that the enhancement of the copper signal was related to the chloride concentration of the medium: instead of the usual decrease of the copper wave with chloride concentration observed in DPASV (12), it was found that chloride concentrations in the range 0.02–0.1 M caused enhancement of the SWASV copper signal. The effect was not investigated further but is probably kinetic in nature since the frequency of the potential waveform applied to the working electrode differed considerably between DPASV and SWASV (in the present study: 1 Hz and 125 Hz, respectively). The enhancement effect was not observed with low- and medium-thickness NCTMFE, but reappeared with a high-thickness NCTMFE.

Several interesting observations can be made from Table I:

(a) Coating of the glassy carbon electrode with a low-thickness Nafion film resulted in a startling increase in the lead and cadmium signal when recorded with SWASV and, to a lesser extent, with DPASV. With higher film thicknesses,

Table II. Effect of Nafion Coating on the Peak Potential and Peak Width in SWASV

	Cd		Pb		Cu	
	E_p^a /mV	$W_{1/2}^b$ /mV	E_p /mV	$W_{1/2}$ /mV	E_p /mV	$W_{1/2}$ /mV
TMFE	-660	54	-474	54	-170	64
low-thickness NCTMFE	-689	59	-508	59	-160	56
medium-thickness NCTMFE	-689	64	-508	60	-160	64
high-thickness NCTMFE	-689	69	-508	69	-155	69

^a Potentials are given relative to Ag/AgCl. ^b $W_{1/2}$ peak width at half maximum. Experimental conditions are given in Table I.

the signals decreased and with a high-thickness NCTMFE, the sensitivities for lead and cadmium were lower than those observed at a conventional TMFE.

(b) For copper, a low-thickness Nafion coating caused a moderate increase of the DPASV signal, whereas the SWASV signal was decreased; however, the latter effect is probably caused by the abovementioned enhancement of the SWASV signal of copper at the TMFE. Indeed, in the absence of chloride in the electrolyte medium a low-thickness NCTMFE also caused enhancement of the SWASV signal of copper. Highest sensitivity was usually obtained with a medium-thickness film and the signals diminished with further increases in film thickness. (As mentioned above, the copper signals in Table I measured with the high-thickness NCTMFE are unusually large.)

(c) With the exception of the SWASV signal of copper at the TMFE, the magnitudes of the square-wave and differential-pulse signals generally followed the same trend as a function of Nafion film thickness although the changes in the square-wave signals were much more dramatic than those seen in the differential-pulse signals.

(d) The magnitude of the linear-sweep voltammetric signals only varied slightly as a function of film thickness for either of the metals. In theory, the LSASV signal is a direct measure of the amount of metal accumulated in the mercury phase during deposition. Therefore, this result indicates that the relationship between the peak heights measured with the differential techniques and the thickness of the Nafion film cannot be accounted for by differences in preelectrolysis efficiency.

In Table II, the peak potentials and peak widths of the SWASV signals for cadmium, lead, and copper at the TMFE and the NCTMFE are given. A low-thickness Nafion coating shifted the peak potentials of cadmium and lead approximately 30 mV in a negative direction relative to those at the uncoated electrode, indicating that the coating indeed constitutes a separate phase which interacts with the stripping process. For copper, a small positive peak shift was observed. Further increases in the Nafion film thickness did not affect the peak potentials noticeably. For lead and cadmium, Nafion-coating resulted in some peak broadening which increased with film thickness. For copper, a low-thickness NCTMFE yielded a slightly sharper peak than the TMFE; however, with increasing film thickness, the peak was again broadened.

The effects of Nafion coating on the peak potentials and peak widths in DPASV and LSASV followed the same trends as those described for SWASV.

The relatively constant values of the LSASV peak heights in the absence and presence of Nafion films indicate that the membrane coating does not significantly hinder the transport of metal ions to the electrode surface during deposition. Calculation of the diffusion layer thickness δ at the RDE with conditions typical for the present study (diffusion coefficient of metal ion, 10^{-5} cm²/s; kinematic viscosity of electrolyte medium, 10^{-2} cm²/s; rotation speed, 500 rpm) yields a value for δ of 2×10^{-3} cm. Thus, the Nafion coatings are considerably thinner than the diffusion layer. The data available on diffusion of metal ions in bulk Nafion (e.g., ref 13) show

that the diffusion coefficients in the polymer phase are somewhat lower than those in aqueous solution. However, owing to the radical procedure used to dissolve the bulk Nafion, the recast films will undoubtedly be more hydrated than the bulk phase and will not hinder diffusion to the same extent. Experimentally, the transport properties of the Nafion coating were investigated by recording Levich plots (i.e., signal magnitude as a function of (rotation rate)^{1/2}). In the range of rotation speeds available (500–3000 rpm) the stripping signals increased with the rate of rotation, and correlation coefficients of 0.985, 0.988, and 0.988 were obtained for cadmium, lead, and copper, respectively. Thus, in spite of the Nafion coating, the limiting step in the overall mass transport during deposition is still the convective-diffusive transport of analyte in the solution.

Most likely, the enhancement of the SWASV and DPASV signals at the low-thickness NCTMFE is due to more efficient replating of metal ions when the applied pulse ceases as the film coating will confine the newly oxidized ions to the immediate vicinity of the electrode surface. This explanation also accounts for the fact that greater enhancement is seen with SWASV than with DPASV as the pulse repetition rate is much faster in the former method, allowing the analyte to undergo more redox cycles during the stripping scan.

However, the fall-off in signal observed between a medium- and high-thickness film indicates that other effects are operative. It is interesting to note that the SWASV signals obtained with the high-thickness film NCTMFE in two ways resembled those measured at the conventional TMFE. First, the order of the peak heights of cadmium, lead, and copper when measured with SWASV (i.e., $I_{Cu} > I_{Pb} > I_{Cd}$) was the same, whereas the order was different with the low- and medium-thickness NCTMFE. Second, the unusual effect of chloride concentration on the SWASV peak height of copper at the TMFE reappeared at the high-thickness NCTMFE but was not seen at the thinner Nafion coatings. These findings strongly indicate, that the electrode process at the high-thickness NCTMFE is more susceptible to solution chemistry effects than at the thinner coatings. No experimental evidence was obtained which could further elucidate this phenomenon, but a plausible explanation is simply that a partial opening of the polymer structure takes place between the medium- and high-thickness NCTMFE, leaving the mercury phase more exposed. Also, the loss in sensitivity for cadmium and lead in SWASV and DPASV at the high-thickness NCTMFE can be accounted for in this manner, as a larger fraction of the newly oxidized metal will escape from the vicinity of the electrode surface before the pulse is reversed, and the sensitivity gain accruing from multiple deposition/stripping cycles of the analyte will diminish. Furthermore, the hypothesis is supported by the fact that macroscopic cracks appeared in the high-thickness NCTMFE which implies that contractive forces are present in the polymer film. With increasing film thickness, these forces become stronger in comparison with the Nafion/glassy carbon interaction, and the polymer sheet is under stress.

The cracks observed at the high-thickness NCTMFE did not affect the performance of the electrode as it exhibited the

peak shifts typical of Nafion coating and showed much greater insensitivity to surface-active compounds than the TMFE.

Nafion coating was not found to affect the size and shape of the ASV background signal noticeably in chloride-free solutions. However, in chloride-containing media, the commencement of the oxidation wave of chloride was shifted positively (cf. Figure 1), thus expanding the useful potential range. In the standard medium employed, containing 0.05 M chloride, the potential shift observed in the SWASV voltammograms was approximately 100 mV. The reason for this effect is probably that the Nafion coating to some extent repels anions and therefore lowers the effective chloride activity at the electrode surface.

Being an ion-exchange resin, Nafion is capable of preconcentrating metal ions on its own. Thus, prior to the application of the preelectrolysis potential, the Nafion coating may already have accumulated an amount of trace metal ions which to some extent will be amalgamated once the reductive plating potential is imposed on the electrode. In order to assess the significance of this mechanism relative to the direct diffusion of metal ions through the membrane, an experiment was performed in which a NCTMFE without any applied potential was allowed to equilibrate with a solution containing 2×10^{-7} M cadmium, lead, and copper. Subsequently, a square-wave scan from 0 V to -900 mV was performed in order to measure the amount of metal incorporated in the Nafion. In the absence of Nafion coating no metal reduction wave was seen, indicating that the metal ion concentrations are too low to be determined by the direct voltammetric method. In the presence of Nafion, signals from cadmium, lead, and copper (in particular the latter) were clearly discernible. However, the peak currents obtained in this manner were, at the most, 5% of those obtained in an SWASV experiment performed on the same sample with 60 s deposition at -900 mV vs. Ag/AgCl. It can therefore be concluded that, with the very thin Nafion coatings employed, the cation-exchange preconcentration mechanism is insignificant in comparison to diffusion of metal ions through the film during the deposition step in ASV.

The sensitivity in SWASV of different NCTMFEs prepared with the same procedure (i.e., coating of the glassy carbon electrode and subsequent deposition of mercury) could vary by a factor as high as 3. This finding indicates that the formation of the Nafion phase during the evaporation of the applied polymer solution plays a significant role in the performance of the electrode. Two correlations between the visual appearance of the Nafion coating and the sensitivity were observed. First, sensitivity tended to increase with the extent of the central, refractive zone. Second, an irregular refraction pattern in the central zone resulted in higher sensitivity than a regular, concentric pattern. The microscopic reason for this behavior is not known.

Once prepared, the NCTMFE showed excellent reproducibility. Repetitive DPASV signals ($n = 8$) measured with 30-s preelectrolysis at -1.0 V vs. Ag/AgCl in a solution containing 1.0×10^{-7} M of cadmium, lead, and copper resulted in relative standard deviations of the peak currents of 4.2%, 4.2%, and 5.0%, respectively.

The linearity of the responses was examined with DPASV at a low-thickness NCTMFE. In the first experiment, the metal ion concentrations were varied between 1 and 80 nM with the experimental conditions $E_{\text{dep}} = -1000$ mV, $t_{\text{dep}} = 120$ s, and pulse amplitude = 50 mV. In a second experiment, the metal concentrations were varied between 0.1 and 2.0 μ M with the instrumental parameters $E_{\text{dep}} = -1000$ mV, $t_{\text{dep}} = 10$ s, and pulse amplitude = 10 mV. The correlation coefficients obtained in the first and second experiment (in parentheses) were 0.9995 (0.994), 0.997 (0.998), and 0.990 (0.996) for cad-

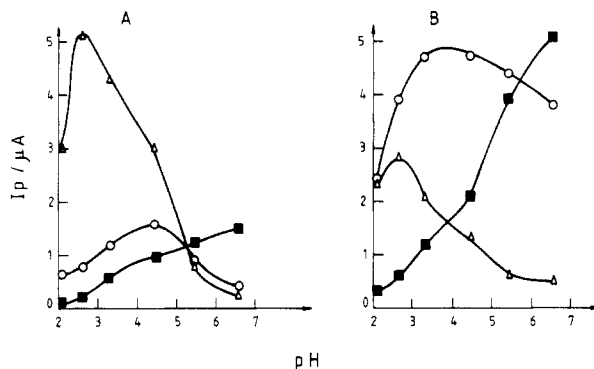


Figure 2. Effect of pH on the SWASV peak current of cadmium (■), lead (○), and copper (Δ) at (A) TMFE and (B) low-thickness NCTMFE: 2.0×10^{-7} M metal ion; preelectrolysis for 60 s at -900 mV vs. Ag/AgCl; initial medium composition, 0.02 M NaAc, 0.05 M NaCl. pH-variation was obtained by titration with concentrated nitric acid.

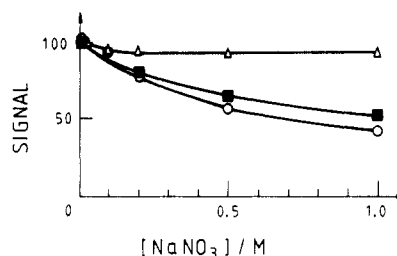


Figure 3. Effect of ionic strength on SWASV peak currents of cadmium (■), lead (○), and copper (Δ). Peak currents are given relative to those obtained with no added sodium nitrate. Experimental conditions were as follows: 2×10^{-7} M metal ion; preelectrolysis for 60 s at -900 mV vs. Ag/AgCl; initial medium composition, 0.07 M acetate buffer, 0.05 M sodium chloride.

mium, lead, and copper, respectively. At concentrations higher than 2 μ M, nonlinearity (i.e., saturation effects) became evident. In conclusion, the NCTMFE exhibits linear response and is analytically useful over a wide concentration range.

Figure 2 shows the pH dependence of the stripping peak currents of cadmium, lead, and copper at the TMFE and the NCTMFE. With both electrodes, cadmium shows a steady decrease in sensitivity with decreasing pH, while lead and copper show maximum sensitivity at intermediate pH values. For lead, the pH values of the maximum differ somewhat between the TMFE and the NCTMFE (pH 4.3 and 3.8, respectively). The effect of ionic strength on the response of Nafion-coated electrodes was tested by addition of an inert electrolyte to the standard medium. At the TMFE, addition of up to 1 M sodium nitrate did not produce any significant change in the peak currents of cadmium, lead, and copper, whereas the signals decreased with increasing ionic strength at the NCTMFE, in particular for cadmium and lead (Figure 3). The explanation for the latter observation is probably that the diffusion coefficients of counterions in ion-exchange materials normally increase with the ionic strength of the contacting solution (14). Consequently, during the stripping step in the differential ASV techniques the newly oxidized analyte will diffuse further away from the electrode surface before the pulse is reversed, and the signal enhancement owing to multiple plating/stripping cycles of the analyte will be diminished. Another possible explanation is simply that the morphology and the geometrical parameters of the Nafion microstructure change as a function of the ionic strength of the contacting solution (15).

Effect of Surfactants on the ASV Response of the NCTMFE. The effect of surface-active organic compounds on the ASV response at the NCTMFE was examined by using cadmium as test analyte. For comparison, the surfactant effect

Table III. Effect of Surfactants on the SWASV Peak Current of Cadmium for the TMFE and the NCTMFE

surfactant	electrode type	Δi_p (%) at the following surfactant concn				
		1 ppm	2 ppm	5 ppm	10 ppm	20 ppm
Triton X-100	TMFE	+4	-11	-41	-66	^a
	NCTMFE	+2	+6	-11	^b	-16
sodium dodecyl sulfate	TMFE	0	-11	^b	^b	-33
	NCTMFE	+4	-1	-2	^b	-7
dodecylpyridinium chloride	TMFE	-68	^a	^a	^a	^a
	NCTMFE	+8	-12	^b	^b	-60
gelatin	TMFE	-18	-40	^b	^b	-54
	NCTMFE	-1	-5	-7	^b	-6
protein standard solution	TMFE	-45	-85	-89	-100	-100
	NCTMFE	0	-3	-11	^b	-16
octanol	TMFE	+2	+12	+11	^b	-4
	NCTMFE	0	+1	-2	^b	-5

^aSignal poorly defined or interfered with by tensammetric peaks. ^bSignal not measured at this surfactant concentration. Experimental conditions: [Cd(II)] = 2.0×10^{-7} M, preelectrolysis for 60 s at -90 mV vs. Ag/AgCl; electrode rotation rate, 500 rpm. High-thickness NCTMFEs were used except for protein standard solution (low thickness).

on the conventional TMFE was also recorded. The six surfactants chosen were nonionic (Triton X-100), anionic (sodium dodecyl sulfate), and cationic (*n*-dodecylpyridinium chloride) detergents, a colloidal protein (gelatin), a protein standard solution (albumin and globulin in the weight ratio 5:3), and a long-chained alcohol (1-octanol).

As seen in Table III, the NCTMFE is much less susceptible to peak depression than the TMFE in the presence of detergents, especially with Triton X-100 and dodecylpyridinium chloride. Whereas the latter caused severe peak depressions at the TMFE in concentrations as low as 1 ppm, much higher concentrations could be tolerated with the NCTMFE. In addition, the signal quality is higher at the NCTMFE. For instance, with Triton X-100 present in concentrations higher than 5 ppm, a tensammetric peak strongly interfered with the cadmium signal at the TMFE, whereas no such effect was seen at the NCTMFE (Figure 4).

It is interesting to observe that the extent of peak depression at the NCTMFE caused by detergents is in the order cationic > nonionic > anionic. Other things being equal, this sequence would be expected from the cation-exchange properties of Nafion in that cations more easily penetrate a negatively charged membrane than do neutral molecules or—in particular—anions. Moreover, it has been shown that Nafion has a remarkably high affinity for hydrophobic cations (16), which probably accounts for the fact that dodecylpyridinium chloride causes larger peak depression at the NCTMFE than any of the other surfactants tested. The NCTMFE also showed a better response than the TMFE in the presence of protein. Indeed, with the protein standard solution the difference in performance was remarkable; whereas 1 ppm protein almost halved the cadmium signal at the TMFE, addition of 8000 ppm protein only caused a 60% signal reduction at the NCTMFE. However, at this concentration level of organic matter it cannot be said whether the peak depression is caused by the interaction of the protein with the electrode process or by secondary effects such as complexation of the analyte and changes in the viscosity of the medium.

1-Octanol did not affect the cadmium signal significantly, either in the presence or absence of a Nafion coating on the electrode.

Application of NCTMFE in Analysis of Urine Samples. The analytical utility of the NCTMFE was assessed by applying it to the determination of trace metals in untreated urine. This matrix poses considerable problems in electroanalysis due to its high organic content and it also affected the performance of the NCTMFE. Addition of urine to a 0.5 M hydrochloric acid solution resulted in a drop in sensitivity for cadmium, lead, and copper. At the low pH of this medium,

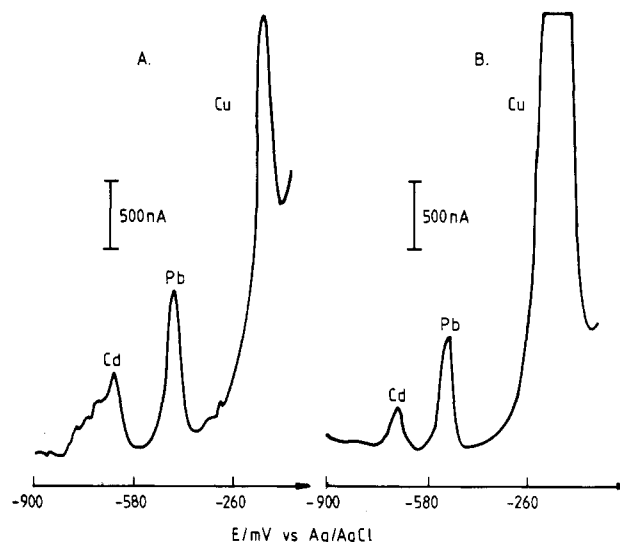


Figure 4. Square-wave stripping signals obtained with (A) TMFE and (B) high-thickness NCTMFE in solution containing 5 ppm Triton X-100. Experimental conditions are as given in Table III except that the sample was also spiked with 2×10^{-7} M Pb(II) and 2×10^{-7} M Cu(II).

complexation of the trace metals by constituents of the urine matrix is unlikely, and the signal depression can therefore be attributed to adsorption of organic matter on the working electrode. Direct analysis of undiluted urine samples with the TMFE or the NCTMFE did not prove feasible as adsorption of organic matter took place to the extent that a brownish tinge developed on the cell walls and on the RDE. Although well-defined stripping signals could be obtained, the signal magnitude decreased during repetitive ASV scans in the urine matrix. However, the interference effects could largely be remedied by 1/3 dilution of the urine sample with water. Figure 5 shows stripping voltammograms of cadmium, lead, and copper obtained under such conditions. Generally, in order to release bound trace metals, sample acidification is desirable for total metal determination but the loss of sensitivity for cadmium at low pH (cf. Figure 2) was found to be prohibitive. However, it has been shown previously (17, 18) that the cadmium and lead responses measured in urine at pH 4–6 reflect total metal. The lead content of the undiluted urine sample was found to be 25 nM, while the cadmium signal, although discernible, was not a significantly higher than the blank signal. At pH 5.5, no sensible recovery of copper spikes could be obtained in the urine samples, probably due to solution chemistry effects. Acidification to pH 1.0 greatly increased the copper signal, and it responded to standard

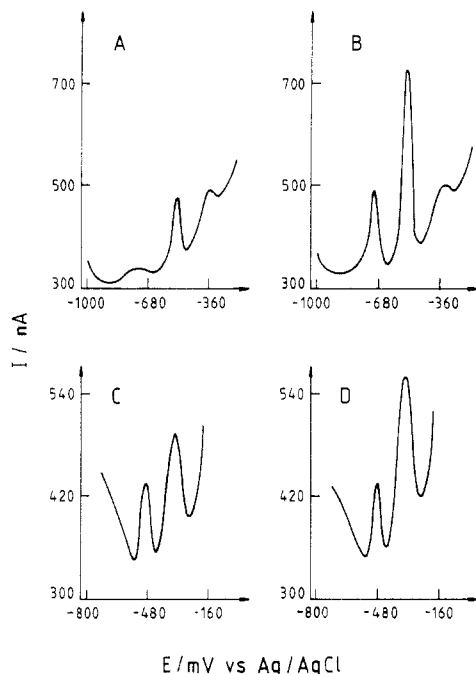


Figure 5. DPASV signals of cadmium, lead, and copper obtained with high-thickness NCTMFE in an untreated, diluted urine sample: (A) pH 5.5, preelectrolysis for 60 s at -1000 mV vs. Ag/AgCl; (B) as (A) spiked with 5 nM Cd(II) and 12.5 nM Pb(II); (C) pH 1.0, preelectrolysis for 60 s at -800 mV; (D) as (C) spiked with 50 nM Cu(II).

additions at this pH. The copper concentration of the urine sample was found to be $0.33 \mu\text{M}$, which is in reasonable agreement with the value obtained by inductively coupled plasma spectroscopy ($0.29 \mu\text{M}$). Occasionally, crazing of the polymer coating occurred when low-thickness Nafion films were exposed to the acidified urine matrix. This problem did not occur with the high-thickness NCTMFE, which therefore was preferred for this application.

Although the NCTMFE was not insensitive to the organic constituents of the urine matrix, its performance was far superior to that of the TMFE. With the latter, a noisy background signal was obtained, and the cadmium and copper signals were often interfered with by unidentified peaks, probably due to redox processes or adsorption/desorption of sample constituents. At the NCTMFE, no such phenomena were observed, and the quality of the ASV signals was higher. At present, further research is being carried out to assess the utility of the NCTMFE for routine analysis of clinical samples.

CONCLUSION

The above results show that the application of the NCTMFE in stripping analysis is very promising. The electrode modification not only offers considerably higher resistance to organic interferences than the TMFE but also yields higher sensitivity when used in conjunction with su-

perimposed differential waveforms. Another important advantage of the NCTMFE is the mechanical stabilization of the mercury film. At present, work on the preparation of Nafion films with improved properties is under way. In particular, recast films which reconstitute the properties of the bulk polymer would be desirable as the latter is completely insoluble in organic solvents at ambient temperature and pressure. Recent progress in this area has been reported (19).

However, it must be appreciated that membrane coating of the working electrode cannot possibly eliminate all organic interferences in ASV. Even if the interfering species are prevented from reaching the electrode surface and thus cannot give rise to tensammetric waves or redox signals, they may still deposit on the outside of the membrane and affect mass transport. For ASV analysis of samples with high organic contents, electrode regeneration between each measurement may therefore be inevitable. As recently reported (20), this approach can be fully automated with the conventional TMFE when implemented in a flow system. In the case of the NCTMFE the renewal of the Nafion coating cannot be automated, but rinsing of the electrode surface with a suitable solvent may prove sufficient.

Registry No. Cd, 7440-43-9; Pb, 7439-92-1; Cu, 7440-50-8; C, 7440-44-0; Hg, 7439-97-6; Nafion, 39464-59-0; Triton X-100, 9002-93-1; sodium dodecyl sulfate, 151-21-3; dodecylpyridinium chloride, 104-74-5; 1-octanol, 111-87-5.

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