

# Some Analytical Properties of the Nafion-Coated Mercury Film Electrode

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The signal of the mercury film electrode modified by a Nafion film at the differential pulse anodic stripping voltammetry of trace metals and adsorptive stripping voltammetry of nitrazepam has been investigated. The polymer membrane deposited by simple casting from 1 % ethanol—water solution enhances significantly the signal stability, in particular at the determination with the sample solutions exchange. The coating restricts also a fouling effect of the dodecyl sulfate anion (up to the concentration  $2 \text{ g dm}^{-3}$ ) and the hyamine cation (within  $\text{mg dm}^{-3}$ ). The sensor was applied to the analysis of food samples.

The mercury film electrode (MFE) is still a typical voltammetric indicating electrode used both at a batch procedure and in flow-through cell [1]. The mercury film can be simply prepared electrolytically (*ex situ* or *in situ*) and it ensures a high sensitivity of the determination. The conventional mercury electrode, however, suffers strongly from surface-active compounds [2]. To encourage a direct application of the MFE in analysis of complex matrix samples, various chemical modifications of the MFE by semipermeable polymeric membranes have been suggested [3, 4]. Among them, the commercially available negatively charged perfluorinated polymer Nafion was widely tested and the Nafion-coated mercury film electrode (NCMFE) was used for the determination of heavy metals in body fluids [5, 6], waters [7, 8], milk [9], minerals [10], waste waters and sludges extracts [11]. A mechanical stabilization of the mercury film at the NCMFE owing to the immobilization of the mercury droplets in the polymer matrix was also observed [12].

The simple droplet evaporation of a diluted alcohol—water Nafion solution on the solid electrode substrate followed by the deposition of the mercury phase is usually employed for the preparation of the NCMFE. Recently, a poor signal stability of such NCMFE has been mentioned and the importance of casting solvent as well as curing the Nafion film at high temperature has been reported [12].

We were, therefore, interested in comparison of the signal stability of the MFE and NCMFE prepared in the usual manner. The aim of the study was an investigation of the Nafion effect on the electrode signal at the repeated measurement as well as at the determination without and with an exchange of sample solution in the absence and in the presence of surfactants.

The differential pulse anodic stripping voltammetry (DPASV) and differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV) were employed as the detection techniques for the determination of trace metals and nitrazepam, respectively. The anionic dodecyl sulfate (DODS, the sodium salt) and the cationic hyamine (HYA) were used as interfering surfactants. The NCMFE was applied to the analysis of food products.

## EXPERIMENTAL

All chemicals were of reagent grade. Test solutions ( $1 \times 10^{-6} \text{ mol dm}^{-3}$  copper, lead, and cadmium and  $7.4 \times 10^{-6} \text{ mol dm}^{-3}$  nitrazepam (Slovakofarma, Hlohovec) in  $0.1 \text{ mol dm}^{-3}$  acetate buffer of pH 4.5) were prepared freshly before use. Deionized and double distilled water was used throughout.

The solution of honey (VČELPO s. r. o. OBORA, Skalica nad Svitavou) was prepared by dissolution of 1 g of honey in  $50 \text{ cm}^3$  of distilled water.  $5 \text{ cm}^3$  of this solution were pipetted into the electrolytic cell and  $20 \text{ cm}^3$  of acetate buffer solution were added. The test solution of apple drink (NOKO s. r. o., Nové Mesto nad Váhom) was prepared from  $5 \text{ cm}^3$  of the original drink and  $20 \text{ cm}^3$  of acetate buffer solution.

Measurements were performed with a PA-4 polarographic analyzer in conjunction with a Rotating disc electrode assembly (Laboratorní přístroje, Prague). The electrodes employed were a rotating glassy carbon electrode (3 mm diameter), a platinum auxiliary electrode, and a saturated calomel reference electrode. Nafion was obtained from Aldrich as a 5 mass % solution.

The NCMFE was prepared as described previously

[11]. Briefly, 2 mm<sup>3</sup> drop of 1 % Nafion solution (in ethanol—water,  $\varphi_r = 1 : 1$ ) was placed on a mirror-polished glassy carbon electrode and the solvent was allowed to evaporate for about 10 min at room temperature. Then, the mercury film was deposited from the  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup> mercury nitrate solution in 0.1 mol dm<sup>-3</sup> acetate buffer of pH 4.5 by the electrolysis at  $-1.0$  V *vs.* SCE for 8 min. The electrode was renewed daily by wiping with a soft tissue and fresh preparing.

At the determination of metals, the solution was deaerated for 10 min with argon and the DPASV measurement was performed at the conditions as follows: electrode rotation 1150 min<sup>-1</sup> during the deposition step, deposition potential  $-1.0$  V, deposition time 120 s, rest time 20 s, scan range from  $-1.0$  V to 0.05 V, scan rate 10 mV s<sup>-1</sup>, modulation amplitude 12.5 mV; pulse repetition rate 0.2 s.

For the determination of nitrazepam the solution was deaerated and the accumulation of the analyte was done at  $-0.2$  V in a stirred solution for a given time. After 10 s rest, the working electrode potential was scanned from  $-0.2$  V to  $-0.8$  V at the scan rate 20 mV s<sup>-1</sup>, modulation amplitude 50 mV.

## RESULTS AND DISCUSSION

The Nafion coating used enhances the sensitivity of the measurement. Compared to the MFE, the NCMFE yielded about twofold values of the DPASV peak currents. The stripping peaks of Cu, Pb, and Cd were shifted to the negative potentials by 6 to 10 mV. This can be explained by the cation-exchange properties of the polymer membrane.

The signal stability of the electrodes has been examined by 20 repeated simultaneous measurements of Cu, Pb, and Cd in one and the same solution. The repeatability data expressed by the relative change of the peak currents between the 1st and the 20th measurements and by the relative standard deviation (RSD) of the peak currents are summarized in Table 1. The positive (negative) value of the relative signal change indicates an increase (decrease) in the signal going from the 1st to the 20th measurement. A significant improvement of the signal stability for the NCMFE in the absence of the DODS surfactant can be seen. In the presence of the tenside the stability of the NCMFE signal is evidently worse.

Fig. 1 shows the DPASV peak current values obtained with the same MFE and NCMFE at the measurement with the exchange of the test solutions. Six test solutions of the same composition ( $1 \times 10^{-6}$  mol dm<sup>-3</sup> metals) have been analyzed with 6 repeated measurements in each solution. A low stability of the MFE signal can be seen although the signal values of all metals for the individual measurements correspond quite well. A significantly higher signal stability was obtained with the NCMFE, in particular from

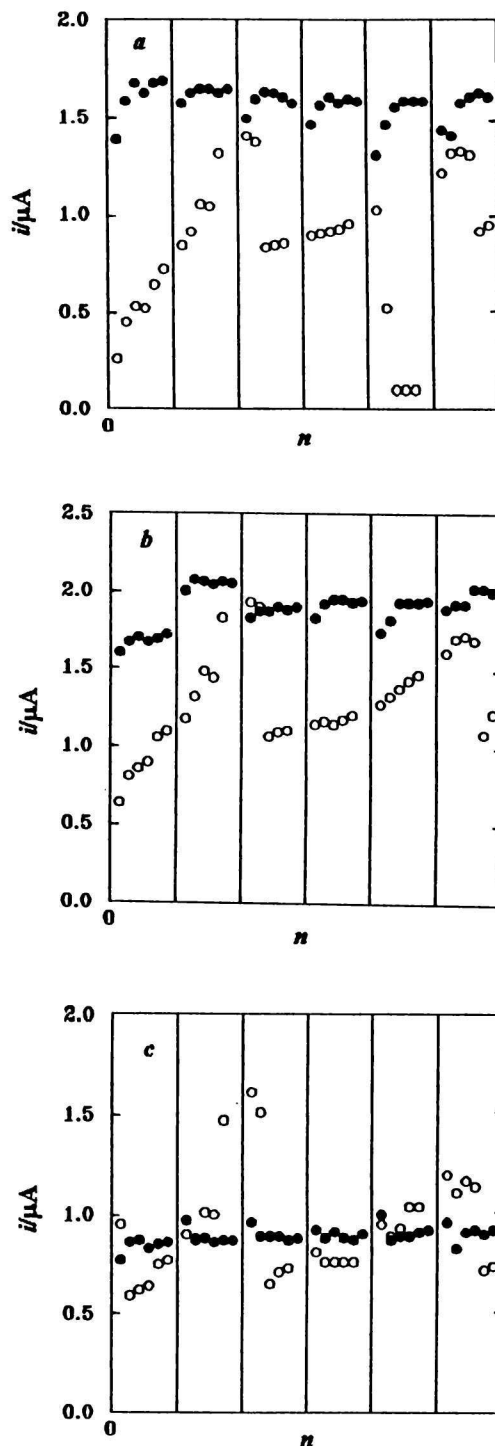


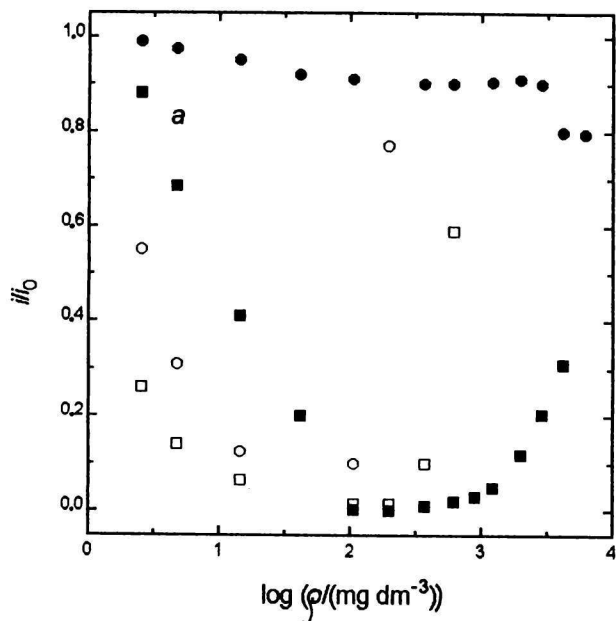
Fig. 1. The DPASV peak current values for repeated measurements ( $n = 6$ ) in six test solutions of the same composition with the same MFE (o) and NCMFE (●).  $1 \times 10^{-6}$  mol dm<sup>-3</sup> Cd (a), Pb (b), and Cu (c).

the 4th to the 6th measurements in each solution. The NCMFE signal is relatively stable also at the exchange of the test solutions both in the absence and in the presence of the DODS surfactant (Table 2). This behaviour of the NCMFE confirms a stabilizing effect of

**Table 1.** Signal Stability for 20 Repeated DPASV Measurements in One and the Same Solution.  $1 \times 10^{-6}$  mol dm $^{-3}$  Metals in 0.1 mol dm $^{-3}$  Acetate Buffer of pH 4.5

Electrode	Dodecyl sulfate $\rho$ /(mg dm $^{-3}$ )	Signal change/% <sup>a</sup> (RSD/%) <sup>b</sup>		
		Cd	Pb	Cu
MFE	–	19.0 (5.6)	10.6 (3.5)	10.9 (3.9)
NCMFE	–	– (1.3)	– (1.4)	– (1.8)
NCMFE	10	–11.8 (4.8)	4.4 (2.0)	–13.3 (5.4)
NCMFE	1000	– (4.1)	17.7 (6.3)	– (3.2)

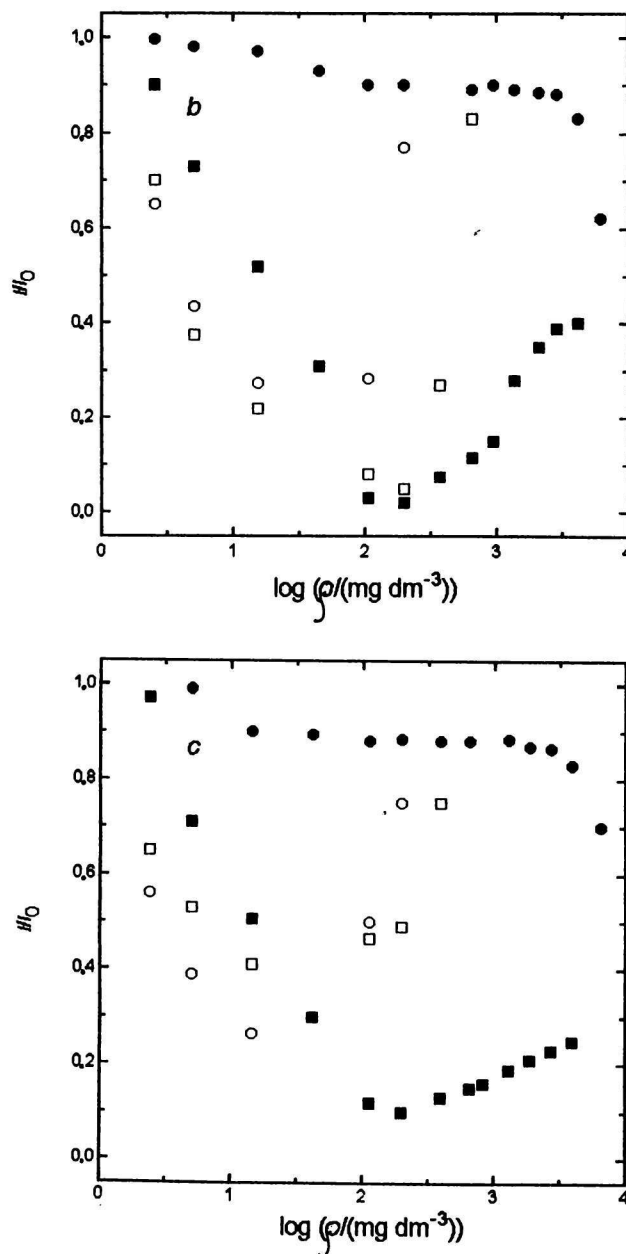
a) Relative change of the DPASV peak current between the 1st and the 20th measurement,  $100(i_{20} - i_1)/i_1$ . b) Relative standard deviation of the DPASV peak current ( $n = 20$ ).


**Table 2.** Signal Stability for 6 Repeated DPASV Measurements with the Same Electrode in Six Test Solutions of the Same Composition (Total  $n = 36$ ).  $1 \times 10^{-6}$  mol dm $^{-3}$  Metals in 0.1 mol dm $^{-3}$  Acetate Buffer of pH 4.5

Electrode	DODS $\rho$ /(mg dm $^{-3}$ )	RSD/%		
		Cd	Pb	Cu
MFE	–	45	14.9	20.2
NCMFE	–	2.7	6.8	2.3
NCMFE	10	4.0	5.7	2.2
NCMFE	1000	6.3	4.1	5.2

the Nafion film on both mechanical as well as chemical properties of the mercury phase.

Another important feature of the Nafion membrane is its semipermeability. This was examined at the determination of the trace metals in the presence of the DODS anion and the HYA cation. The performance of the MFE and the NCMFE in the presence of the ionic surfactants is shown in Fig. 2. An excellent


**Fig. 2.** Dependence of the normalized DPASV peak current at the MFE (○, □) and the NCMFE (●, ■) on the concentration of DODS (○, ●) and HYA (□, ■). The  $i_0$  represents the peak current in the absence of the surfactants.  $1 \times 10^{-6}$  mol dm $^{-3}$  Cd (a), Pb (b), and Cu (c).

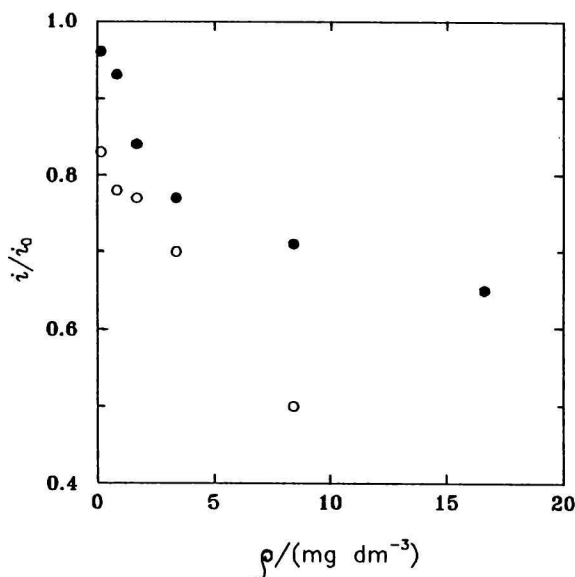


Fig. 3. Dependence of the normalized DPAdCSV peak current of  $7.4 \times 10^{-6}$  mol dm<sup>-3</sup> nitrazepam in acetate buffer of pH 4.6 on the concentration of DODS. MFE (○), NCMFE (●).

barrier effect of the Nafion membrane can be seen, in particular towards the negatively charged dodecyl sulfate up to the concentration of 2 g dm<sup>-3</sup>. The NCMFE can also restrict hyamine at a low concentration similarly as it was observed for the nonionic surfactants [11]. It can be seen that the Nafion film preserves also the electrode from an adsorptive accumulation of metals at high concentration of the tensides (totally for DODS and partially for HYA).

The linear calibration graphs (the correlation coefficients > 0.998) were obtained at the NCMFE for the metals within the concentration ranges  $1.2 \times 10^{-8}$  to  $1.5 \times 10^{-7}$  mol dm<sup>-3</sup> and  $1.2 \times 10^{-7}$  to  $1.5 \times 10^{-6}$  mol dm<sup>-3</sup>. The linearity did not change in the presence of 10 mg dm<sup>-3</sup> and 100 mg dm<sup>-3</sup> DODS for the lower and higher metal concentration range, respectively.

The food products, honey and apple drink, dissolved in acetate buffer were analyzed utilizing the NCMFE. In honey solution, the trace metals concentration was near to the blank values. The addition of copper ions indicated their complexation by the honey matrix. The recovery of the copper determined for this sample after the spike addition ( $2 \times 10^{-9}$  mol) and its equilibration was about 100 %.

A strong copper complexation was also observed for the apple drink test solution. The concentration

of lead and cadmium was determined at the NCMFE using the method of two standard additions. The contents of lead and cadmium recalculated for the original apple drink ( $0.015$  mg dm<sup>-3</sup> Pb and  $0.002$  mg dm<sup>-3</sup> Cd) are below the allowed values. The application of the MFE to this sample was unsuccessful for a high background current.

An application of the NCMFE for the adsorptive cathodic stripping voltammetry was also tested. Nitrazepam was determined as a model compound using the adsorptive accumulation—voltammetric stripping scheme, where the substance yields the cathodic peak at  $-0.51$  V. The nitrazepam signal vs. accumulation time dependence is linear up to 60 s for  $7 \times 10^{-6}$  mol dm<sup>-3</sup> nitrazepam and then starts to level off. An interfering effect of the surface-active compound DODS is shown in Fig. 3. While at the uncoated electrode the DODS strongly competes with nitrazepam, the NCMFE exhibits discriminative properties. Thus the simple *in situ* separation effect of Nafion at the electrode surface can be utilized also at the determination of electroactive organic compounds.

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