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DETERMINATION OF HYDROGEN PEROXIDE WITH SENSORS BASED ON HETEROGENOUS CARBON MATERIALS MODIFIED WITH MANGANESE DIOXIDE

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Three different types of MnO_2-modified electrodes were investigated on their electrochemical response towards hydrogen peroxide: a bulk-modified carbon paste electrode, a film-modified carbon paste electrode and a film-modified screen printed electrode. The sensors were characterized by voltammetric (cyclic voltammetry, linear sweep voltammetry) and amperometric methods (stationary and flow conditions). The best responses were obtained with a MnO_2 film-modified screen printed carbon electrode which could be used as an electrochemical detector in flow injection analysis (FIA) using a NH_3/NH_4Cl buffer (0.2 M, pH 9.5) as a carrier. With FIA a detection limit (3σ) of 0.26

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$\mu g\ l^{-1}$ could be achieved; the peak current was linear to the H_2O_2 concentration from 1 to 200.000 $\mu g\ l^{-1}$. The method could be successfully applied to the determination of H_2O_2 in various samples (cosmetic and medical products, rain water). With flow injection a sample frequency of 60 h^{-1} can be achieved.

Introduction

The development of sensors plays an important role in electroanalytical chemistry [1,2,3]. To increase the selectivity and the limit of detection, modification of the electrodes is widely applied [3]. For electroanalytical purposes, mainly glassy carbon, carbon pastes, carbon inks, porous carbon films or noble metals are suitable substrates which can be modified. Carbon paste as inexpensive, non-poisonous electrode material is simple to modify and therefore used by electroanalytical chemists [4-7]. Conductive carbon inks can be printed in thick film technology on an electrochemically inert supporting material (mainly polymers or ceramics). Modification of the ink allows a design of disposable sensors especially tailored for the analyte of interest and for decentralized inexpensive analysis [8-10].

Hydrogen peroxide (H_2O_2) is an intermediate in biological and environmental reactions with omnipresent character [11-14]. In most cases the long-term stability of the analyte in the sample is a major problem [12,13]. Therefore fast analysis with a minimum of sample pretreatment is required.

Flow injection analysis (FIA) combined with an amperometric detection can be a proper analytical arrangement for a fast determination of hydrogen peroxide. For this purpose modified electrodes are most commonly applied because they allow to lower the overpotential of H_2O_2 significantly [4,6,7]. In this respect particularly carbon paste electrodes (CPEs) are frequently used due to their ease of modification. Catalysts (mediators) for the electrochemical oxidation or reduction of H_2O_2, such as noble metals, metal oxides and metal complexes are either introduced into the carbon matrix by direct mixing or deposited as a film onto the electrode surface [15-17].

Manganese dioxide powder as a mediator can easily be added to carbon paste as well as to carbon ink [15,16]. Film formation of MnO_2 onto carbon supports is best done by electrodeposition via anodic oxidation of manganese(II) from a bulk solution [16,18].

In this paper the analytical performance of different MnO_2-modified carbon supports will be elucidated.

Experimental

Apparatus

Batch Experiments

Batch investigations with carbon paste were carried out with a polarograph PAR 174A (EG&G Princeton Applied Research, Princeton, New York, USA), combined with a universal programming unit (model PARC 175, EG&G Princeton Applied Research). The cell compartment was a self-constructed electrode assembly of Plexiglass, [19] equipped with a titration vessel of glass (6.1415.220, Metrohm, Herisau, Switzerland) and a platinum wire as the counter electrode. The Ag/AgCl reference electrode (6.1227.000, Metrohm) was in contact with the solution *via* a salt bridge (1 M KCl) equipped with a Vycor frit. A magnetic stirrer and a Teflon-coated stirring bar (approx. 300 rpm) provided the convective transport. Registration of voltammetric curves was either done on an X–Y recorder (RE 0089, EG&G Princeton Applied Research) or on a personal computer with an appropriate interface for analogue to digital conversion [20].

Voltammetric studies with screen printed electrodes (SPEs) were performed with an electrochemical work station (BAS 100B Bioanalytical Systems Inc., West Lafayette, Indiana, USA). The cell compartment (model C2, BAS) was equipped with a glass vessel (20 ml), a platinum wire as the counter electrode and a Ag/AgCl reference electrode (3 M NaCl, MF 2063, BAS). The data were evaluated by the corresponding software (BAS 100 W, version 2).

Flow Injection System

The flow-injection system consisted of a high performance liquid chromatographic (HPLC) pump (Model 510, Waters, Milford, MA, USA), a sample injection valve (U6K, Waters), and a thin-layer electrochemical cell. Teflon spacers (MF-1047, MF-1048, BAS) were used to adjust the thickness of the flow-through cell. An Ag/AgCl electrode (3 M KCl, model RE-1, BAS) served as the reference. The counter electrode was the back plate of the cell, made of stainless steel.

For the carbon paste electrodes the commercially supplied electrode body was used. Two electrodes were operated in parallel configuration (total electrode surface 0.14 cm^2). Currents were recorded with a potentiostat BAS, LC-4C. If they were higher than 50 μA, a potentiostat PAR 174A was used. The data were registered with a strip chart recorder (X–Y 7KC 1924-8AD, Pharmacia Fine Chemicals, Uppsala, Sweden).

Screen printed electrodes (SPEs) were fixed *via* the Teflon gaskets directly to the back plate of the thin layer cell with a Teflon support as a holder. The

total electrode surface was 0.40 cm^2. The currents obtained with SPEs were recorded with the electrochemical work station BAS 100 B.

Reagents and Solutions

Deionized water was distilled twice in a quartz still and then purified with an ion exchange system (Nanopure Barnstead, Dubuque, Iowa, USA). Hydrogen peroxide (p.a., 30% Merck) was standardized by iodometric titration [21]. An aqueous stock solution containing 10,000 mg l^{-1} H_2O_2 was prepared freshly each day. Solutions of lower concentrations were prepared immediately before use. All chemicals were of analytical grade. Ascorbic acid, citric acid, and hypoxanthine were from Fluka (Buchs, Switzerland), manganese dioxide and other chemicals from Merck.

Ammonia/ammonium chloride buffer (pH 9.5) was prepared by dissolving 5.349 g of ammonium chloride (p.a., Merck, Darmstadt, BRD) and 7.5 ml ammonia 25 % (p.a., Merck) in water and making up to 1000 ml. This solution served as supporting electrolyte for batch voltammetric analysis after deaeration with argon as well as carrier for FIA after deaeration with helium.

Working Electrodes

Carbon Paste Electrodes (CPEs)

Batch voltammetry. A Teflon rod (11 mm outer diameter) with a hole at one end (7 mm diameter, 3 mm deep) for the carbon paste filling served as working electrode body. Electrical contact was made with a platinum wire through the center of the rod. Unmodified carbon paste was prepared by adding 1.58 g paraffin oil (Uvasol, Merck) to 5.00 g spectral carbon powder (RWB, Ringsdorff-Werke, Bad Godesberg, BRD). A MnO_2 bulk-modified carbon paste was prepared by substituting 5 % (m/m) of the carbon powder by manganese dioxide and then adding the paraffin oil. The mixture was homogenized carefully and allowed to rest at least for 24 hours. The carbon paste was packed into the hole of the electrode and smoothened with a PTFE spatula. For the preparation of a film-modified CPE a MnO_2 film was electrodeposited onto the surface of an unmodified CPE from a deaerated ammonia/ammonium chloride buffer solution containing 20 mg l^{-1} Mn^{2+} (as chloride) with a potential of 0.6 V applied for 60 min under convection. The resulting MnO_2-film electrode was rinsed carefully with highly pure water.

Flow injection analysis (FIA). When using bulk modified carbon paste the corresponding electrode material was filled into the electrode holes of the thin layer cell and smoothened with a PTFE-spatula. In the case of the film modification, MnO_2 was electrodeposited onto the surface of the plain carbon

paste electrodes. After assembling the amperometric cell was flushed with a deaerated ammonia/ammonium chloride solution containing 20 mg l^{-1} Mn^{2+} (as chloride) with a flow rate of 0.5 ml ml^{-1} and an applied potential of 0.6 V for 60 min. After film formation water was used as carrier for 5 min; afterwards again ammonia/ammonium chloride buffer was used as carrier. Alternatively the film can be generated under analogous batch conditions before assembling the cell, leading to identical results.

When using the modified CPEs for FIA measurements, the electrodes were activated once a day by repeating ten times application of a potential of -0.8 V and 0.4 V for 30 seconds each and scan to the negative potential.

Screen Printed Electrodes (SPEs)

Screen printed electrodes were produced from carbon ink (No. C50905DI, Gwent, Pontypool, UK) and laser pre-etched ceramic supports (113 × 166 × 0.635 mm, No. CLS 641000396R, Coors Ceramics GmbH, Chattanooga, TN, USA). The preparation consisted of applying thick layers (0.05 mm) of the ink onto the substrates through an etched stencil with the aid of a screen printing device (SP-200, MPM, Franklin, Ma, USA). The resulting plates were dried at 60 °C for one hour. Isolation was performed by brushing an insulating layer of nail slick onto the surface of the screen printed electrode so that an area of 10 mm^2 was left unisolated. The electrical contact was made with a crocodile clamp. The film formation was carried out as explained with carbon paste electrodes. For the film-modified SPEs no activation was necessary.

Procedures

Batch Voltammetric Measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV). CV and LSV were carried out with a scan rate of 20 mV s^{-1}. For pH values other than the basic electrolyte adjustment was done with NaOH or HCl. After 15 s of equilibration cyclic voltammograms were recorded from 0.8 V to -1.5 V, linear sweep voltammograms from 0.4 V to -0.8 V.
Hydrodynamic Amperometry (HA). Hydrodynamic amperograms were recorded at a working potential of 0.46 V.

Flow Injection Analysis

Unless otherwise stated FIA was carried out with an applied potential of 0.46 V vs. Ag/AgCl. The usual flow rate was 1.0 ml s^{-1}, the injection volume 50 µl.

Evaluation of the responses is best done by their heights.

Analysis of Samples

Medical solutions containing H_2O_2 (Bio-Garten; Köttmannsdorf, Austria) and blonding boosters (Spray Blond; Chattem, UK) were diluted 1:1000 (v/v) and 1:2500 (v/v), respectively, with water and analyzed by the FIA method.

Rain water samples were collected in August 1996 and in August 1997 in Graz, Austria. All samples were stored in a refrigerator and, if necessary, diluted with the carrier solution immediately before use. The samples were analysed by means of the flow injection method.

The concentration were evaluated with the help of calibration curves and by adding internal standards.

Results and Discussion

Cyclic Voltammetric Behavior of H_2O_2 at MnO_2-Modified Heterogenous Carbon Supports

Figure 1 illustrates the cyclic voltammetric behavior of hydrogen peroxide at MnO_2-modified carbon electrodes.

At a plain CPE the reduction of oxygen-containing groups of the carbon particles appears at -1.2 V, overlapped by the reduction of electrolyte components at even more negative potentials (Fig. 1A, curve a) [15].

MnO_2 bulk-modified carbon paste electrodes show in the cathodic scan a broad reduction wave starting from about -0.2 V, where manganese(IV) is reduced to species in lower oxidation states (Fig. 1A, curve b) [22]. This signal is superimposed at more negative potentials with the response of the plain electrode. With increasing the number of cycles a current decrease of the manganese signal can be observed. Anodic oxidation of the manganese(II, III) species starts at -0.2 V.

The CV of the bulk modified CPE in the presence of H_2O_2 displays a broad reduction signal at -1.0 V due to reduction of MnO_2 and/or H_2O_2, probably assisted by C-O groups of the paste (Fig. 1A, curve c). More distinctly at 0.4 to 0.5 V oxidation of manganese(II/III) can be observed. This signal is increased by increasing the concentrations of H_2O_2. The characteristic shape of the curve indicates catalytic mediating action of MnO_2 towards H_2O_2.

The film-modified CPE shows, in the presence of H_2O_2, a broad reduction at around 0 V in the first cycle which disappears subsequently (Fig. 1B, curve d). It is assigned to the reduction of surfacial hydroxide of manganese in high oxidation states > II. At around -1 V another broad reduction signal is discernible. It is probably caused by electrochemical transformation of MnO_2

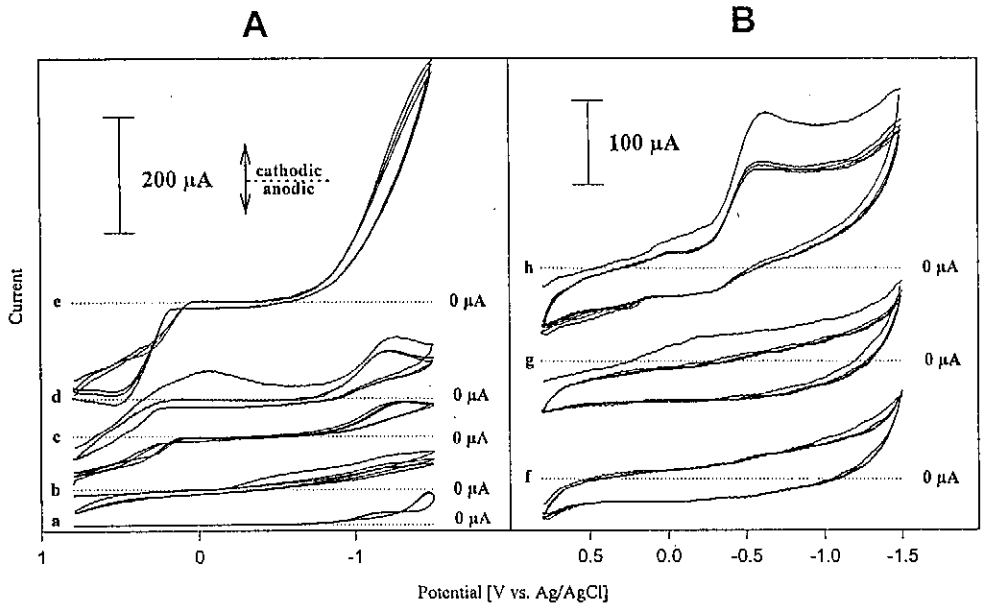


Fig. 1 Cyclic voltammograms of unmodified and MnO_2-modified carbon paste (A) and screen printed electrodes (B); plain CPE (a), bulk-modified CPE (b, c), film-modified CPE (d, e), plain SPE (f), film-modified SPE (g, h); H_2O_2 concentrations: 0 mg l^{-1} (a, b, d, f, g), 50 mg l^{-1} (c, e, h); equilibration time: 30 s, initial potential: 0.8 V, final potential: -1.5 V vs. Ag/AgCl, scan rate: 20 mV s^{-1}, supporting electrolyte: NH_3/NH_4Cl buffer (0.2 M)

to lower oxidation states. In the positive potential window notable oxidation occurs at potentials > 0.3 V. In general, the film-modified electrode displays higher current than the bulk modified indicating increased activity of the modifier at the electrode surface.

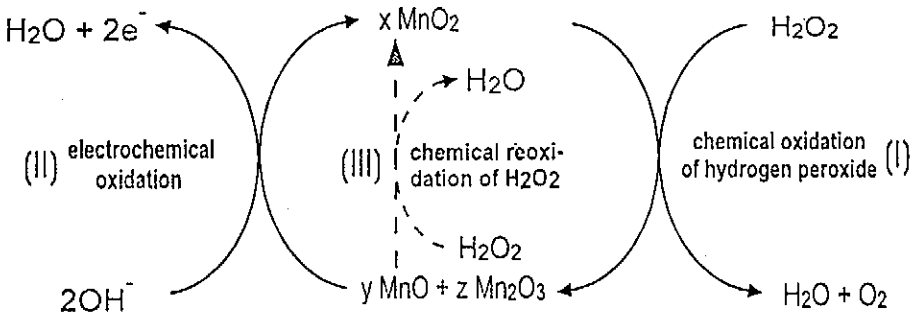
Reduction of H_2O_2 at the MnO_2 film-modified CPE starts at about -0.7 V (Fig. 1A, curve e). The strongly increased current indicates a highly active electrode surface. An oxidation signal occurs at around 0.5 V. The shape of the curve indicates that H_2O_2 is involved in a catalytic process.

A plain screen printed electrode shows a significant current flow over the whole potential range (Fig. 1B, curve a). Probably, residual oxidizable and reducible components of the polymeric matrix produce this relatively high background current.

When modifying the SPE with a film of MnO_2, the electrochemical behavior of the electrode is similar to that of a film-modified CPE, but the signal responses are less distinct (Fig. 1B, curve b).

When H_2O_2 is present in the bulk solution, clearly discernible responses can be monitored. Significant current increases occur below -0.5 V in the negative and above 0.2 V in the positive potential range.

Though all modified electrodes respond to H_2O_2 in the negative as well as in the positive potential range, it was found that the anodic current can be better and more specifically exploited for quantitative analytical determinations. The increase of oxidation currents at potentials > 0.2 V caused by hydrogen peroxide is based on catalytic mediation of MnO_2 and is summarized in the following scheme.



Hydrogen peroxide reacts chemically with the mediator (MnO_2) by formation of H_2O, O_2, and manganese oxides (I); the latter are electrochemically reoxidized, which produces the catalytic current (II). As it can be expected, chemical reoxidation of oxides of manganese in lower oxidation states should also occur (III), which, on the whole, corresponds to a mere decomposition of H_2O_2 catalyzed by MnO_2. Reaction (III) is obviously kinetically slower than (II) because the catalytic activity of the modifier can be electrochemically monitored.

Optimization of the Batch Method

Influence of pH

The influence of pH on the signal was studied with LSV and hydrodynamic amperometry. All modified electrodes gave similar results. When applying voltammetry, the maximum response was obtained with a pH around 9.5. With hydrodynamic amperometry a current plateau was reached between pH 9 and 9.5 and increased with higher values of pH. The best potential for evaluating the catalytic currents was determined to be 0.46 V. Figure 2 shows hydrodynamic amperograms with a film-modified SPE, applying this working potential.

In order to avoid high alkalinity of the solution, a pH of 9.5 was chosen for the subsequent investigations. Low alkalinity is particularly important when using such electrodes for the development of biosensors.

The concentration of the supporting electrolyte also influences the voltammetric response. It is constant with concentrations > 0.2 M buffer (0.1 M NH_3

+ 0.1 M NH_4Cl) but decreases with lower electrolyte concentrations.

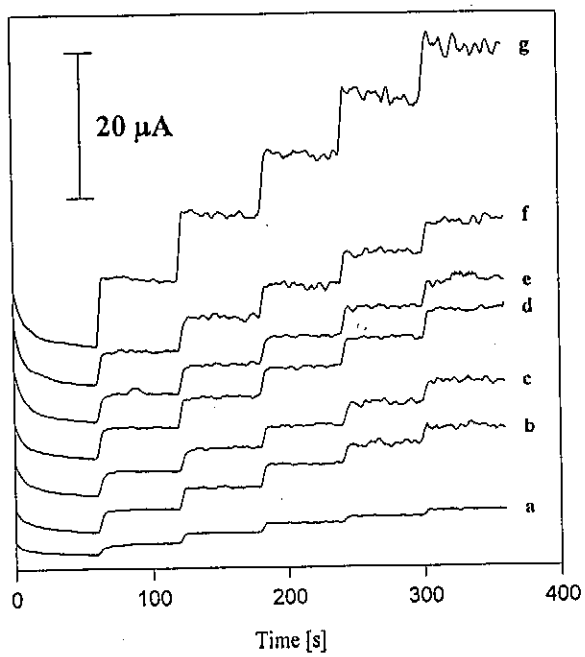


Fig. 2 Hydrodynamic amperograms of H_2O_2 with a MnO_2 film-modified SPE; operating potential: 0.46 V vs. Ag/AgCl, supporting electrolyte: NH_3/NH_4Cl buffer (0.2 M); addition of 10 mg l^{-1} H_2O_2 at the intervals of 60 s; stirring: 700 rpm; pH 7(a), 7.5(b), 8(c), 8.5(d), 9(e), 9.5(f), and 10(g)

Flow Injection Analysis (FIA)

For FIA the supporting electrolyte served as a carrier. As an example characteristic current-time profiles for different H_2O_2 concentrations (a rain water sample without and with spikes) recorded with a MnO_2 film-modified SPE are shown in Fig. 3.

All the electrodes respond rapidly to the dynamic changes of the H_2O_2 concentration in the carrier. No response was observed with unmodified sensors.

Working Potential

Figure 4 shows the response obtained with the three types of modified detecting electrodes at different applied potentials.

The smallest peak surface currents were obtained with the bulk-modified electrode, whereas the film-modified ones exhibited better signals. The optimum

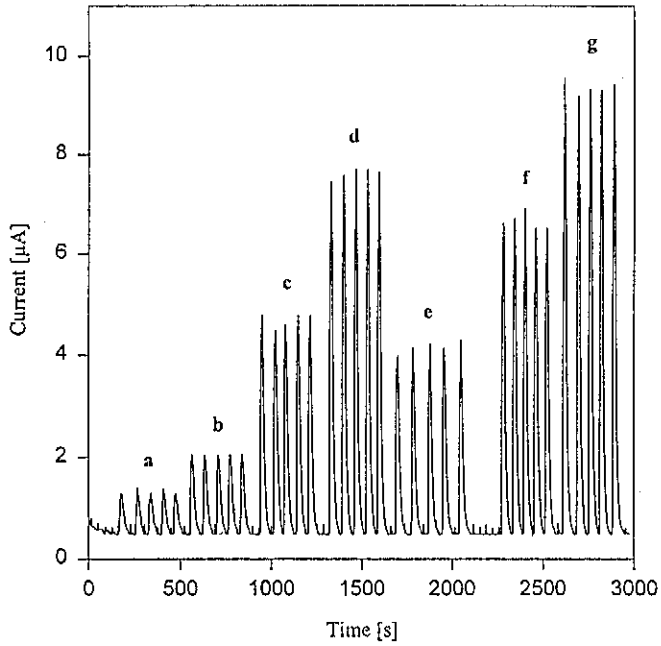


Fig. 3 FIA responses of H_2O_2 of standards and of pure and spiked rain water samples; flow rate: 1.0 ml min^{-1}, working potential: 0.46 V vs. Ag/AgCl, injection volume: 50 μl, carrier: NH_3/NH_4Cl buffer (0.2 M); standards: 100 (a), 200 (b), 500 (c), 800 μg l^{-1} (d), rain water (e), rain water + 300 (f), rain water + 600 μg l^{-1} H_2O_2 (g)

working potential values were found between 0.4–0.5 V. Higher values of operating potential can even exhibit a larger current response but are undesirable due to increased possibilities for oxidation of interferences. The film-modified sensors can be operated even at potentials of 0.2 V and lower, whereas the bulk-modified CPE does not respond to H_2O_2 in this range. The best analytical performance is shown by the film-modified SPE which can be preferably used for quantitative analysis.

Flow Rate Dependence

Investigations into the dependence of the FIA response vs. the flow rate were performed for all three types of electrodes under the injection and steady state conditions. When injecting H_2O_2, an increase of the peak current can be observed with all the modified electrodes up to a flow rate of 1.0 ml min^{-1} whereas it decreases with a higher flux of the carrier. The decrease is due to increased dispersion of the analyte and probably also due to an increased extent of chemical decomposition of H_2O_2 (reaction III in Scheme 1).

If applying steady state conditions (H_2O_2 in the carrier), we get the

response function of a parabolic shape with increasing flow rate f. The cube root of f versus current is not linear indicating that besides the Faradayic process a chemical process is involved, probably catalytic decomposition of H_2O_2 at MnO_2.

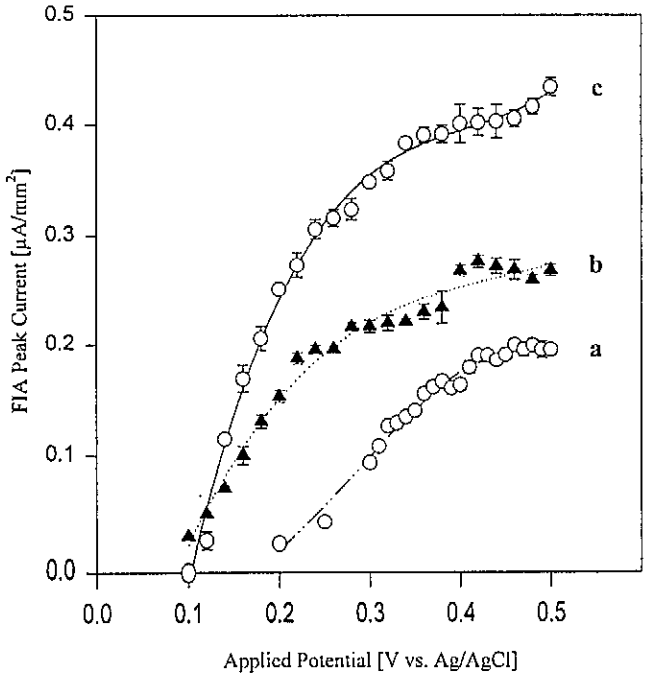


Fig. 4 Dependence of the current response in FIA on the working potential; flow rate: 1.0 ml min^{-1}, injection volume: 50 μl, carrier: NH_3/NH_4Cl buffer (0.2 M); 1 mg l^{-1} H_2O_2 in injected samples

Injection Volume

All modified electrodes show higher currents when increasing the injection volume up to 150 μl above which the responses level off. Volumes of 50 μl - 100 μl show the best analytical performance with respect to analysis time and reproducibility.

Linear Range and Limit of Detection and Reproducibility

The linear ranges and the limits of detection under FIA conditions for H_2O_2 are presented in Table I.

The best results were achieved with the MnO_2 film-modified screen printed sensor. An MnO_2 film-modified glassy carbon electrode operated in

Table I Linear ranges and limits of detection for the amperometric determination of H_2O_2 applying FIA with MnO_2-modified electrodes

	MnO_2 bulk-mod. CPE	MnO_2 film-mod. CPE	MnO_2 film-mod. SPE
Linear range	0.5 - 350 mg l^{-1}	0.01 - 450 mg l^{-1}	0.001 - 200 mg l^{-1}
Limit of detection	3σ = 45 µg l^{-1}	3σ = 0.66 µg l^{-1}	3σ = 0.26 µg l^{-1}

strongly alkaline solutions as described by Wang's group shows a limit of detection of 4 µg l^{-1} H_2O_2, which is slightly higher than the values obtained with the MnO_2 film-modified sensors reported here [18]. The extremely wide range of linear response to H_2O_2 (over 5 decades) for the MnO_2 film-modified sensors presented here make them very promising candidates for the development of biosensors.

Interferences

According to specific requirements of the practical samples, a great number of possible inorganic and organic interferents were investigated [15,16]. In general, substances interfering with the determination of H_2O_2 behave quite similarly at all three modified electrodes. Common electro-inactive cations and anions, such as Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, F^-, Br^- and SO_4^{2-} do not interfere even if they are present in high concentrations. Iron, lead, borate and vanadate interfere significantly when present in concentrations > 20 mg l^{-1}. Copper, hypochlorite, ascorbic acid, uric acid and oxidizable sugars interfere notably even at concentrations in the lower ppm range (5 mg l^{-1}) due to reaction with the analyte and/or the modifier.

Sample Analysis

Various samples containing H_2O_2 were analyzed with the newly developed sensors (Table II)

All the results obtained are in very good agreement with those determined by reference methods or with the values reported in the literature [23]. The H_2O_2 values of rain samples show great variations in their concentration, strongly depending on the photochemical conditions in the air before and during the rain. For the determination of H_2O_2 in rain water it is essential to analyze the samples within a reasonable short time. As it is shown in Fig. 5, decomposition occurs even if the samples are stored in pure polyethylene vessels at 4 °C in darkness.

The concentration of H_2O_2 in rain water decreases to 50 % within one

week. The main reason could be spontaneous decomposition of the analyte due to the presence of heavy metals and dust particles in the sample.

Table II Results of flow injection analysis of samples

Sample	Detectors	Results	Reference method
Blonding booster	MnO_2 bulk-modified CPE	6.23 % ± 0.11	6.21 % ± 0.06, iodometric titration
Medical solution cont. H_2O_2	MnO_2 bulk-modified CPE	2.73 % ± 0.02	2.80 % ± 0.01, iodometric titration
Rain water August 1996	MnO_2 film-modified CPE	5.58 $\mu g\, l^{-1}$ ± 2.0	
Rain water 24.07.1997	MnO_2 film-modified SPE	425 $\mu g\, l^{-1}$ ± 17	
Rain water 01.08.1997	MnO_2 film-modified SPE	46.8 $\mu g\, l^{-1}$ ± 1.0	

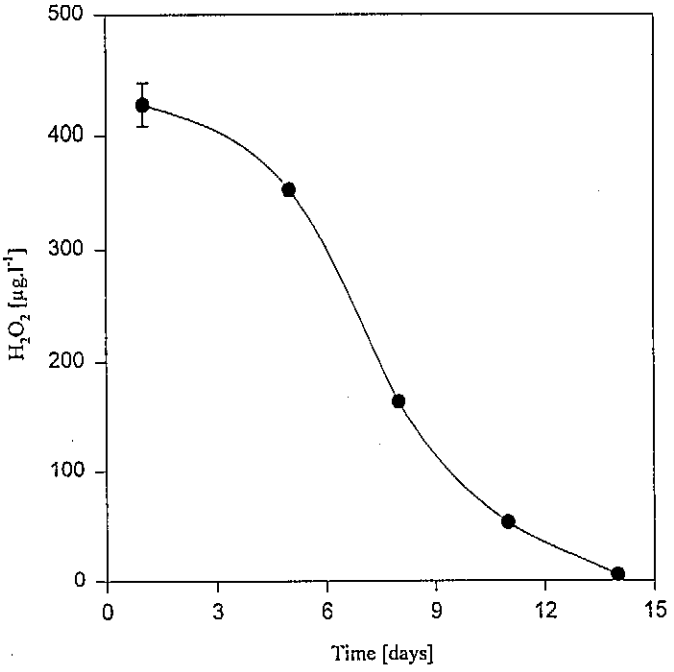


Fig. 5 Decay of hydrogen peroxide in rain water with time, determined with FIA using a MnO_2 film-modified SPE; flow rate: 1.0 ml min^{-1}, working electrode potential: 0.46 V vs. Ag/AgCl, injection volume: 250 µl, carrier: NH_3/NH_4Cl buffer (0.2 M)

Conclusion

The excellent reproducibility and the broad linear range make the MnO_2-modified sensors very suitable detectors for routine analysis by FIA with amperometric detection. Low costs of the chemicals required, simple fabrication and long term stability and the possibility for mass production of disposable strips will focus the industrial use. The new modified CPEs and SPE can be operated even under physiological conditions where additional modification with enzymes (e. g. oxidases or peroxidases) will allow the design of biosensors.

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