

Determination of methylmercury at Nafion[®] coated electrodes by single and multiple pulse voltammetric techniques[☆]

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Abstract

The voltammetric behaviour of methylmercury at Nafion[®] coated glassy carbon electrodes is examined. Cyclic voltammograms recorded at coated electrodes show a dramatic increase of peak currents with respect to bare electrodes, this effect being more evident in perchlorate supporting electrolytes rather than in chloride containing media. Experimental evidence indicates that ion-exchange preconcentration of the cation CH₃Hg⁺ is the prevailing process, even if the incorporation of neutral species such as CH₃HgCl by hydrophobic interactions cannot be neglected. The application and optimization of pulsed techniques like differential pulse voltammetry and Osteryoung's square wave voltammetry, indicates the possibility to use Nafion[®] coated electrodes for the determination of trace methylmercury at submicromolar levels. The analytical performances can be further improved by using, at the Nafion[®] coated electrode, a multiple pulse technique named multiple square wave voltammetry. The application and optimization of this technique to the system under investigation is presented and discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Nafion[®] coated electrodes; Ion-exchange voltammetry; Methylmercury; Multiple pulse voltammetries

1. Introduction

The use of polymer coated electrodes for the ion-exchange preconcentration and determination of redox ions [1,2] has given rise to a new technique named ion-exchange voltammetry [3], which is rapidly widening its application field towards a variety of analytical challenges [4]. It was recently shown that coated electrodes can be used to determine trace concentration of inorganic mercury(II) in natural waters [5–7]. Although

inorganic mercury is highly toxic, methylated forms of mercury are even more dangerous since they can be concentrated through the food chain as a consequence of their high solubility in lipids [8,9]. Methylmercury is the key issue in addressing problems related to human and wildlife exposure to mercury.

Some literature reports deal with the electrochemical behaviour of methylmercury [10–12]. One of these reports concerns the reduction mechanism of methylmercury on a mercury electrode in aqueous solution, which is associated with several chemical reactions and adsorption–desorption processes [10]. It is generally agreed that the polarographic reduction proceeds in two successive one-electron steps, namely, the reversible generation of the methylmercury radical and the irreversible reduction to elemental mercury and methane. The first polarographic wave has analytical significance, giving a linear calibration plot for concentrations between 10⁻⁷ and 10⁻⁴ M [10].

[☆] Dedicated to Jean Clavilier on the occasion of his retirement from LEI CNRS and in recognition of his contribution to Interfacial Electrochemistry.

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Results obtained for the reduction of methylmercury at gold film electrodes [11] indicate that the mechanism may be similar to that proposed for methylmercury at the hanging mercury drop electrode [10]. By exploiting the differential pulse anodic stripping voltammetry with a deposition step at -0.5 V at a gold film electrode in a non complexing medium, and a method of double standard additions for determining methylmercury in the presence of mercury(II) ions, a detection limit of 2×10^{-8} M for methylmercury was achieved.

Agraz et al. [12] proposed the use of carbon paste electrodes modified with a thiolic resin to determine methylmercury. Exploiting the stripping peak after a deposition step at -1 V, a detection limit of 9.3×10^{-9} M has been achieved. However the separation of the methylmercury signal from the inorganic mercury signal is not very specific for methylmercury.

The two prevailing methylmercury species [8] present in acidified waters containing (some) chloride are the CH_3Hg^+ cation and the hydrophobic neutral complex CH_3HgCl ; both species can, in principle, be preconcentrated at electrodes coated with Nafion[®], a perfluorinated cation exchanger [2,3], which is able to preconcentrate also neutral hydrophobic molecules [13]. The detection capabilities of polymer coated electrodes can be improved using sensitive electroanalytical techniques such as differential pulse voltammetry, DPV [14], Osteryoung's square wave voltammetry, SWV [15,16] or new pulsed techniques such as multiple square wave voltammetry, MSWV.

Multiple square wave voltammetry is based on the principle of repeated addition of the integrated transient currents produced after each transition of a multiple potential step sequence applied at the electrode [17,18]. MSWV is a multi-pulse technique which implies a combination of a square wave signal with a staircase waveform, this latter scanning the entire domain of electroactivity of the redox system. This perturbation mode is similar to Barker's square wave voltammetry [19,20] with the difference that onto each step of the staircase, more than one pair of square pulses of opposing sign are applied. Proper sampling of the charge during the pulse sequence allows the improvement of the signal to noise ratio so that it is possible to achieve detection limits lower than those obtained with conventional pulsed techniques.

In the present paper the possibility to preconcentrate and detect trace levels of methylmercury at Nafion coated electrodes (NCE) is examined, together with the possible improvements that the use of multiple pulse voltammetric techniques can give to the analysis.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. Two different methylmercury standard solutions were used: (a) a 3.6×10^{-5} M (9.09 ± 0.2 mg l^{-1}) methylmercury chloride solution in 0.2% HCl and 5% acetic buffer certified by Frontier Geosciences, Environmental Research Corporation, Seattle, USA; (b) solutions prepared by dissolving the proper amount of methylmercury chloride (Alfa Aesar) in 0.1 M HClO_4 .

Milli-Q water was used throughout to prepare the solutions. The measurements were performed in a clean laboratory, under a Class 100 laminar flow hood. All electroanalytical measurements were carried out at room temperature ($22 \pm 1^\circ\text{C}$) under a nitrogen atmosphere. A conventional single compartment cell equipped with a platinum coil counter electrode and a $\text{Ag}|\text{AgCl}|\text{KCl}$ (sat) reference electrode were employed. The working electrode was a PTFE-shrouded glassy carbon disk (area 0.2 cm²) polished to a mirror finish with graded alumina powder.

2.5% w/v Nafion[®] solutions were prepared by 1:1 dilution with methanol of 5% w/v Nafion[®] solutions (Aldrich). Nafion[®]-coated electrodes were prepared by droplet evaporation of 3 μl of the 2.5% w/v Nafion[®] (film coating 0.375 mg cm⁻²). Solvent evaporation was performed in a methanol atmosphere in order to achieve a slow evaporation rate.

Preconcentration of methylmercury was carried out under open circuit conditions in stirred solution (200 rpm with a magnetic stirrer).

2.2. Electrochemical instrumentation

Cyclic voltammetric measurements were performed using a Amel Model 553 potentiostat connected to an Amel Model 568 function generator and a X-Y recorder Yokogawa Model 3023. Differential pulse and Osteryoung's square wave voltammetry were performed with a EG&G PAR Model 384 B polarographic analyser. Multiple square wave voltammetry was performed using a 'MPulse' prototype instrument (see below).

2.2.1. MSW-DD: principles

The principles and the waveform applied to the electrode in MSWV has been presented elsewhere [17,18]. As mentioned in the introduction section, this differential method is an extension of the original concepts proposed by Barker and Gardner [19,20] for DPP and SWV. However, MSWV differs from Barker's SWV by the means used to collect the transient information: instead of the double current sampling operated by Barker, in MSWV the response is built by multiple integration and combination of transient currents.

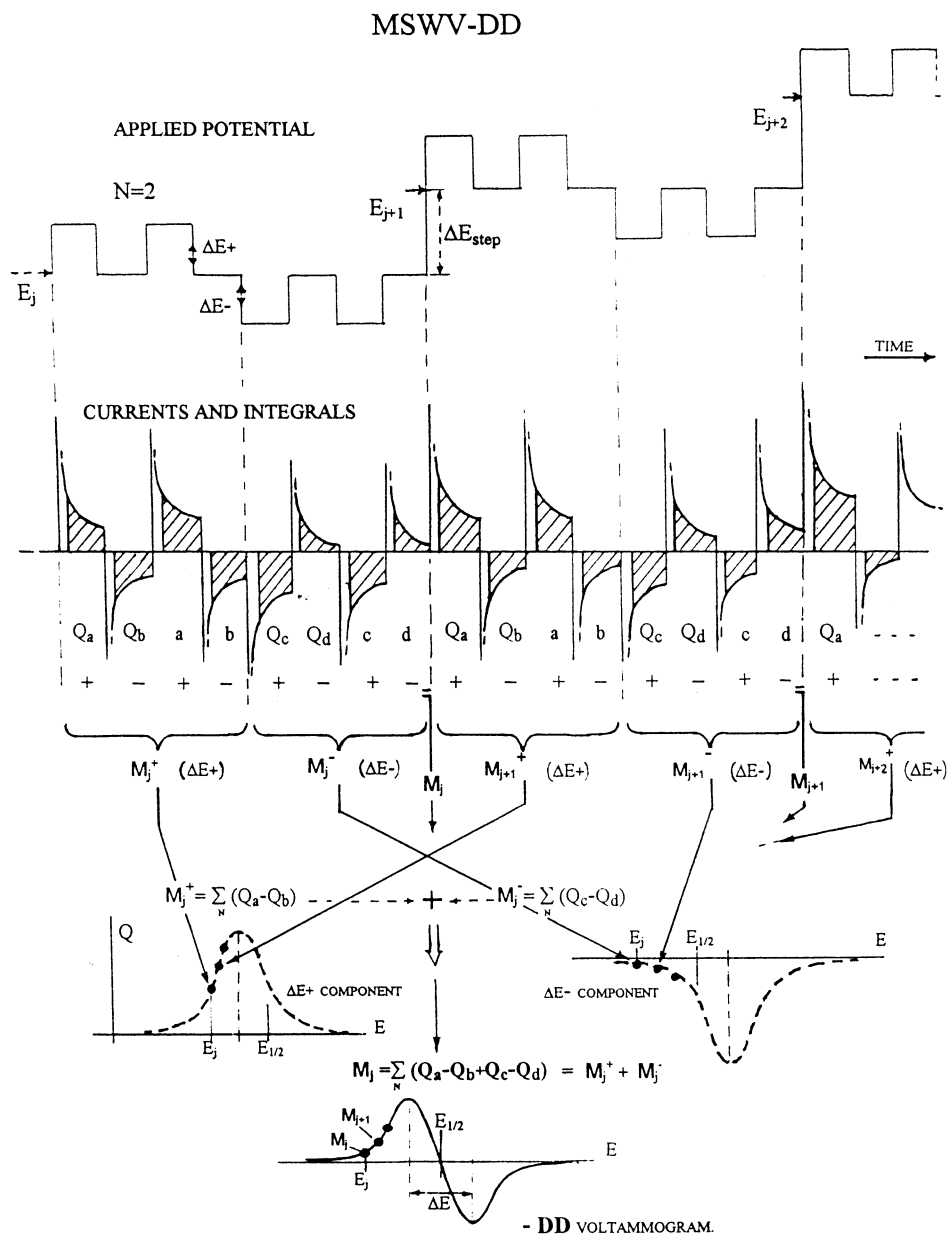


Fig. 1. Multiple square wave voltammetry in the double differential mode (MSWV-DD). The sequence is reduced to $N=2$ with only one inversion of ΔE . The sum (with the indicated signs) of the elements of charges (Q_a, Q_b, a, b, c, d , etc.) corresponding to the $+\Delta E$ pulses produces one component of the response: M_j^+ . The other one, M_j^- comes from the $-\Delta E$ part of the signal, the sum of both, obtained at the end of the step at potential E_j , is one point of the MSWV-DD voltammogram.

It was shown that this technique enhances the signal to noise ratio and the sensitivity [21,22] and can be successfully applied for trace analysis even in complex samples [23–26].

In this work, a new mode of perturbation, named MSW-DD (DD for ‘double differential’) has been developed and widely used. It performs combinations of summations and differences of the multiple integrals in correlation with the polarity of the transitions and with the inversion of the superimposed signal ΔE . The response of this special mode MSW-DD has the shape of the first derivative of the usual mode

(i.e. second derivative of polarographic wave) and offers a better signal to noise ratio [22].

Other studies on comparable approaches for obtaining a second derivative (of the polarographic wave) have been reported [27,28]. They are essentially based on the idea of triple potential step voltammetries; however, in these works, the perturbing signal applied on each step of the staircase is a successive triple level of potential. The repeated sequences of multiple perturbations are not used and the response is formed by samples of the transient currents.

The principles of the MSW–DD method are detailed hereafter and shown in Fig. 1. The underlying idea is to apply at the electrode sequences of pulses containing series of alternate positive and negative potential jumps. The synthesis of the DD response signal comes from the following point: one can consider, in a first approximation, the overall response as the sum of two components corresponding to the series of the $+\Delta E$ and $-\Delta E$ perturbations. These two components are of opposite polarity and their individual peak potential values are separated by ΔE following the relation $E_{\text{peak}} = E_{1/2} - \Delta E/2$ (which is valid for MSWV [17] as well as for DPV and SWV [29]), where $E_{1/2}$ is the polarographic half-wave potential of the electrochemical system under analysis, supposed here to be reversible.

In particular, during the application of the sequence composed of $2 \times N$ perturbations, a delay time after each ΔE is used to impose on the electrode a special potential pulse controlled by the circuits, in order to minimize the time for charging the double layer. During the following time interval, the transient current is integrated by a precision circuit (analog or digital). During the half alternating periods the same integration is carried out, but with an opposite sign, leading to the addition of the integrals. The summation of the $2 \times N$ elements of charge gained with the positive going pulses, constitutes the measured charge M_j^+ . The same process is performed on the negative going perturbations.

The response signal M_j is given by the algebraic summation of the components M_j^+ and M_j^- measured at each potential E_j of the staircase. Note that this value is obtained in the real time of one step of the experiment, no further numerical or mathematical treatment is responsible for the gain in signal to noise ratio. The response is generated only by the specific piecewise combination of the electronically integrated transient currents.

The derivative response is built, as indicated on the scheme, from the combination of multiple elements of the integrated current transients which are in practice averaged and correlated over a rather short time window. The resulting effect is a final level of noise which is lower than the noise observed in the normal mode of MSWV (i.e. simply differential). This low noise is clearly related to the time scale of one application of the multiple perturbations, i.e. to the production of one point of the overall response.

Under favorable conditions of concentration, the base line of MSW–DD becomes (close to) zero, while in the worst cases—like ultra trace analysis far below the ppb range—the baseline of the DD response is (close to) a sloping straight line. This is the result expected by operating the derivative of the baseline of the MSWV response which is (close to) a parabola (as

well as for SWV, under similar conditions). The background component obtained by MSW–DD is then simple to subtract or to compensate automatically and allows one to improve further the real sensitivity of the measurement.

In practice MSW–DD minimizes the effects of a wide spectrum of ‘noises’; it acts on the electrochemical components (the baseline) as well as it performs an inherently fast, real time filtering and averaging on each datum point of the voltammogram, within the crucial time scale (between 10 μs and 100 ms) where the main noises (electrochemical and mechanical fluctuations, electrical or electronic perturbations due to unperfected signals and to the closed loop potentiostatic system, current conversion amplifiers, etc.) may appear.

Indeed, this simplified explanation and the figure help in understanding the principles and give a good semiquantitative estimate of the responses obtained with MSW–DD. The real situation is not so simple. Because of the change in the boundary conditions after each transition, the calculations of the currents after multiple steps of potential of one polarity (i.e. the normal MSWV) is rather complicated [17,30,31]; new initial conditions must be recalculated after each pulse, taking into account the effect of all previous steps to solve the equations. Calculations are even more complicated when the signs of the successive sequences are alternately reversed as in MSW–DD and the simple superposition of the effects of the $+$ and the $-\Delta E$ pulses is no longer valid. The concentration profiles are modified at the beginning of each alternate sequence and are very likely to affect the real amplitude of the two components M_j^+ and M_j^- , leading finally to a slightly dissymmetrical shape of the DD response. This response is also widely dependent on the reversibility of the system studied. Similar behaviour was observed and discussed in the case of the triple potential voltammetries presented in the work cited above [27,28]. This notwithstanding, it should be noted that DD responses for reversible systems consist only of linear combinations of diffusive currents and can be hence exploited for analytical purposes.

In practice, the peak to peak amplitude of the DD voltammogram, for a given and unmodified set of experimental parameters and conditions, stays proportional to the concentrations of the electroactive species in a wide domain which often extends over 3 (or more) decades [22].

2.2.2. MSWV–instrumentation

Multiple square wave voltammetric experiments were carried out using a prototype instrument ‘MPulse’, controlled by its own software, which is currently under development for commercial production [21].

This instrument has been designed to perform most of the so-called ‘pulsed methods’ in electrochemistry.

The main characteristics of the assembly, which was especially designed for trace analysis, resides in its high sensitivity. The structure of the MPulse instrument and of its circuits are based on the application of several electronic innovations together with the introduction of new principles in the mode of extraction of the significant parts of the electrochemical signals. This development has been made in order to produce an accurate and low noise response. The system also contains special circuits (and principles) which improve the separation of the faradaic and of the capacitive (parasitic) components resulting in a better signal to background noise ratio. This point, associated with the effect of a repeated multiple integration process (which acts on the measured signal in a similar way as does a synchronous detection mode [21]), leads to a very high sensitivity. This is valid even in the practical case when very weak currents are produced at the electrodes by electroactive species at trace concentration levels. Among the new concepts implemented, DD, the new mode in the manner of forming the final response, detailed in the previous paragraphs, introduces a significant improvement in the 'base line extraction' in these advanced electroanalytical methods.

3. Results and discussion

3.1. Cyclic voltammetric behaviour of methylmercury at a Nafion[®] coated electrode (NCE)

In order to gain general information on the electrochemical behaviour of methylmercury at bare or modified glassy carbon electrodes, cyclic voltammetric (CV) investigations were first carried out.

Fig. 2, full line, shows the CV pattern recorded at 50 mV s^{-1} at a NCE dipped in a 1×10^{-5} M $\text{CH}_3\text{HgCl} + 0.01$ M HClO_4 solution. It is recorded after equilibration of the NCE with the solution, i.e. when the peak currents reach constant values with time; such an equilibration process takes about 15 min in stirred solution. The voltammograms are characterised by a sharp reduction peak (-0.560 V), to which a reoxidation peak (-0.520 V) is associated. The evidence that peak currents at the coated electrode are dramatically higher than those recorded at a bare GCE, shown in Fig. 2, dotted line, indicates the operativity of an efficient preconcentration of the analyte at the coated electrode.

The analysis of the dependence of the reduction peak currents on the scan rate obtained from the voltammograms presented in Fig. 3, shows that I_p increases linearly with v up to scan rates ≤ 50 mV s^{-1} , while at higher scan rates a linear dependence of peak currents on $v^{1/2}$ is observed. This agrees with the cyclic voltammetric behaviour expected for an electroactive species incorporated within the polymeric layer of a Nafion[®]

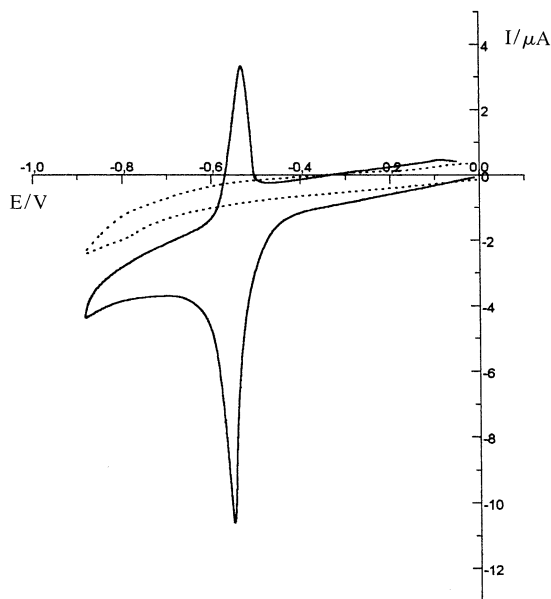


Fig. 2. Cyclic voltammograms recorded at a Nafion[®] coated electrode (NCE) after 10 min of equilibration in 1×10^{-5} M $\text{CH}_3\text{HgCl} + 0.01$ M HClO_4 (full line) and at a glassy carbon electrode (GCE, dotted line). Scan rate 50 mV s^{-1} .

coated electrode [4], observed when the time scale of the ion-exchange process (which is of the order of 10 min) is significantly longer than the time scale of the voltammetric measurement (which is of the order of 5 s). Under these conditions, at low scan rates the film thickness is smaller than the diffusion layer, so that the surface confined electrolysis of all the preconcentrated analyte is performed during the voltammetric scan. On

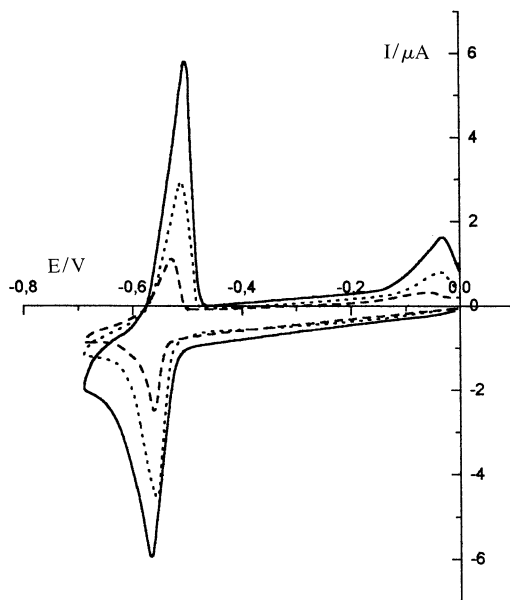


Fig. 3. Cyclic voltammograms recorded at a NCE after 10 min of equilibration in 1×10^{-5} M $\text{CH}_3\text{HgCl} + 0.01$ M HClO_4 at different scan rates: 20 mV s^{-1} (dashed line); 50 mV s^{-1} (dotted line); 100 mV s^{-1} (full line).

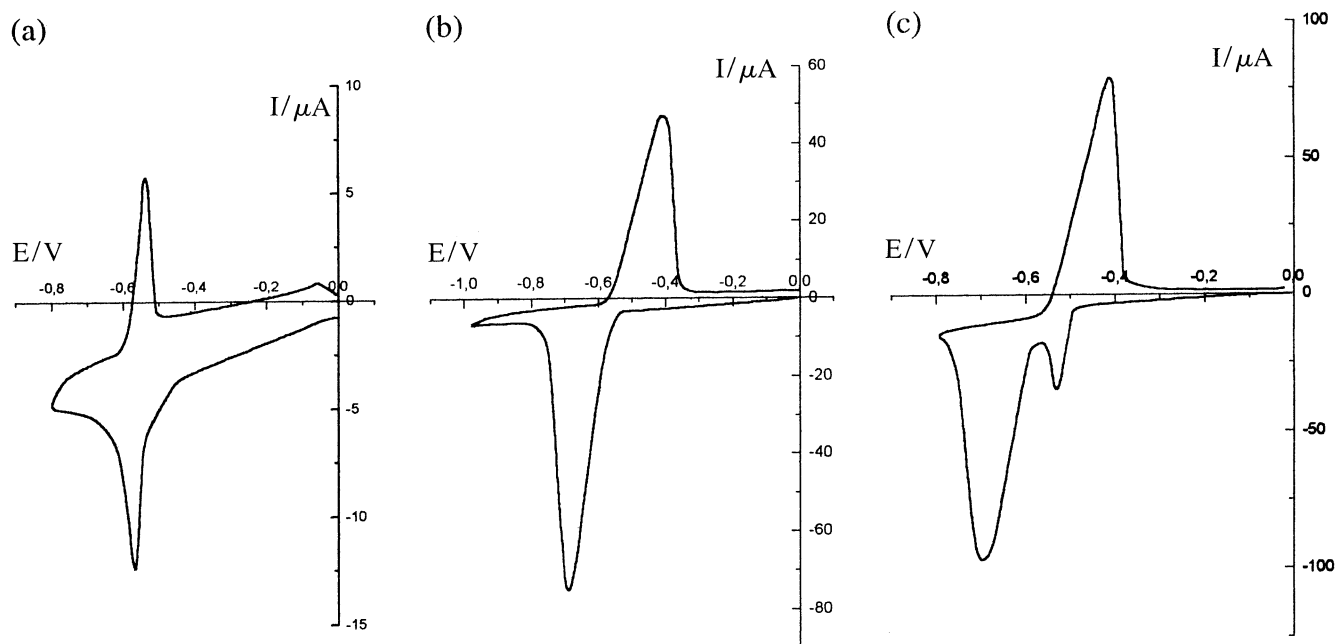


Fig. 4. Cyclic voltammograms recorded at a NCE in 0.01 M HClO_4 after 10 min equilibration in: (a) 1×10^{-5} M CH_3HgCl ; (b) 1×10^{-5} M $\text{Pb}(\text{NO}_3)_2$; (c) 1×10^{-5} M $\text{CH}_3\text{HgCl} + 1 \times 10^{-5}$ M $\text{Pb}(\text{NO}_3)_2$. Scan rate 50 mV s^{-1} .

the contrary, at high scan rates, the diffusion layer is smaller than the film thickness so that a diffusion controlled behaviour is observed. The operativity of a thin-layer like behaviour at low scan rates is confirmed also by the decrease of ΔE_p when $v < 50 \text{ mV s}^{-1}$ (for instance $\Delta E_p = 20 \text{ mV}$ at $v = 20 \text{ mV s}^{-1}$).

An interesting feature of the cyclic voltammetric pattern of methylmercury reduction at the NCE is the difference in the shape of the oxidation and reduction peaks. For instance, at $v \geq 50 \text{ mV s}^{-1}$ the reduction peak shows the tailing typical of a diffusion controlled wave, while the oxidation peak appears sharper, with the shape characteristic of a peak resulting from the destruction of an adsorbed or insoluble film; such a behaviour was previously observed for the reduction of methylmercury at a mercury electrode [10].

It should be noted that at mercury electrodes the reduction of methylmercury takes place at less negative potential values than at the modified glassy carbon electrodes. For instance, Laitinen and coworkers [10] found a peak potential of ca. -0.300 V for the reduction of $4.49 \times 10^{-4} \text{ M}$ methylmercury in 0.1 M HClO_4 , which is significantly less negative than the value recorded at the modified electrode. This shift can be related to the higher energy required to reduce mercury(II) on graphite or glassy carbon electrodes with respect to mercury electrodes [32].

In any case, the reduction peak of methylmercury at the NCE is well resolved from the baseline; this suggests that the reduction peak of methylmercury at the NCE can be exploited for the direct detection of the preconcentrated analyte. It must be emphasised that the

current of this reduction peak increases linearly with the solution concentration, at least up to $5 \times 10^{-5} \text{ M}$ concentration.

The reduction potential of methylmercury at a NCE is close to that of Pb^{2+} [33]; for this reason we examined the effect of the presence of lead(II) on the cyclic voltammetric behaviour of methylmercury at the NCE. As shown in Fig. 4c, the addition of Pb^{2+} causes the overlap of the reoxidation peak relevant to Pb^{2+} alone (see Fig. 4b) with that of methylmercury alone (see Fig. 4a). However, in the direct reduction scan two separated cathodic processes are observed for the two cations. This indicates that the methylmercury reduction peak can be used for analytical purposes also when lead is present in the solution. The higher peak current observed for Pb^{2+} can be explained taking into account that Pb^{2+} is a dication, which is expected to be incorporated in the Nafion[®] coating more efficiently than the monocation CH_3Hg^+ .

Under the experimental conditions described above, Cl^- can form complexes with CH_3Hg^+ . Calculations carried out using literature data [34], lead to the distribution diagram shown in Fig. 5. It is evident that when $\text{pCl} = 5$ the free cation CH_3Hg^+ is 40% of the total methylmercury. In the light of these observations, some experiments with higher chloride concentrations were performed. It was observed that the addition of $1 \times 10^{-3} \text{ M}$ chloride caused a 50% decrease in the methylmercury peak currents, however, a signal still useful for analytical purposes was obtained. Such a decrease in signal agrees with the calculations which indicate that in the presence of chloride concentrations

higher than 10^{-4} M (see Fig. 5) the prevailing methylmercury species is the neutral complex CH_3HgCl . The evidence that a signal is still recorded indicates however that some methylmercury is still present at the electrode|film interface. This suggests that also the neutral complex CH_3HgCl is somehow incorporated by the Nafion[®] coating, probably by hydrophobic interaction. It is worth noting that the incorporation of neutral species within Nafion[®] was proved in the case of ferrocene [14].

3.2. Pulsed techniques

In order to lower the detection limit of the proposed method and to increase the sensitivity of the ion-exchange voltammetric determination of methylmercury, the use of pulsed techniques, such as DPV and SWV, was examined. In all cases no faradaic preconcentration step was carried out, since the incorporation of the analyte in the film by ion-exchange in open circuit condition acted as the preconcentration step.

Fig. 6, full line, shows the DPV pattern recorded after equilibration of the coated electrode in 2×10^{-5} M methylmercury solution. At variance with the signal obtained at a bare GCE (Fig. 6—dashed line) a well resolved reduction peak ($E_p = -0.584$ V) is obtained at the NCE. The effect of the pulse height (PH) on the ratio $I_p/W_{1/2}$ (where $W_{1/2}$ is the peak width at half height) is shown in the insert of Fig. 6. These data indicate that the best pulse height, which gives high peak currents and well resolved peaks, is 50 mV. Peak currents at the NCE increase linearly with methylmercury concentration with a sensitivity of $0.2 \mu\text{A} \mu\text{M}^{-1}$ up to $50 \mu\text{M}$ concentrations. From the background noise ($0.003 \mu\text{A}$, obtained as the standard deviation, σ_b , of five independent background current determinations) by applying the relationship $\text{DL} = 3\sigma_b/m$ (where DL = detection limit and m = sensitivity) [35], a detection limit of 4.5×10^{-8} M is calculated.

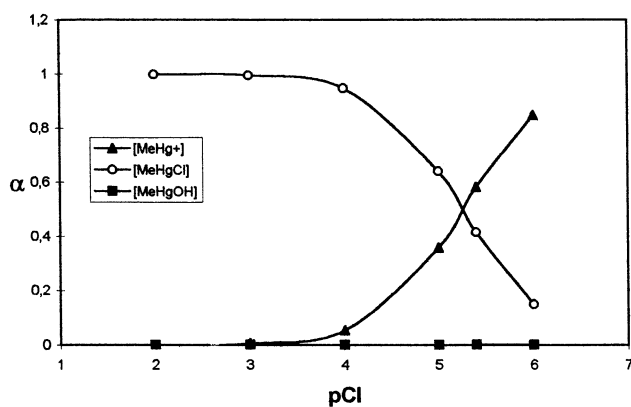


Fig. 5. Distribution diagram for methylmercury as a function of pCl at pH 2.

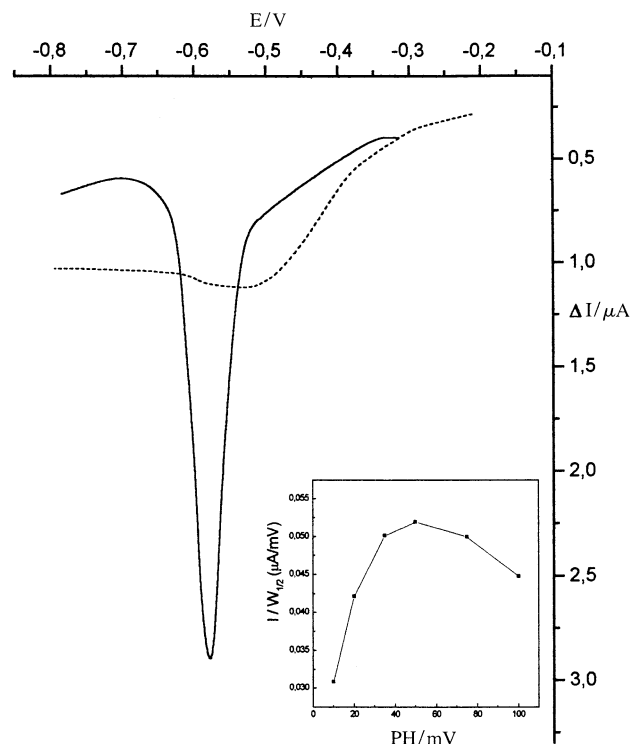


Fig. 6. Differential pulse voltammograms recorded in 2×10^{-5} M $\text{CH}_3\text{HgCl} + 0.01$ M HClO_4 at a NCE (full line) and at a bare GCE (dotted line). Experimental parameters: pulse height 25 mV; scan rate 10 mV s^{-1} ; step time 0.2 s; scan increment 2 mV. Insert: dependence of the ratio between peak current and peak width at half-height on the pulse height.

The presence of chloride causes a decrease of the DPV peak also at the NCE, in agreement with the chloride effect described above for CV.

Fig. 7 shows the SWV patterns recorded at a NCE equilibrated with a 2×10^{-5} M methylmercury solution, as a function of frequency, while keeping constant the pulse height. These data indicate that the peak currents increase with the square root of the frequency, while, at the same time, a small positive shift in the peak potential is observed. The dependence of the $I_p/W_{1/2}$ ratio on the pulse height is shown in the insert in the same figure. The values of 50 mV for the pulse height and 90 Hz for the frequency produce high currents and narrow peaks.

SWV measurements are characterised by a sensitivity about one order of magnitude higher than DPV, probably as a consequence of the positive effect of the increased scan rate on peak currents (the scan rate is higher in SWV).

3.3. MSWV

In order to check the possibility of further improving the sensitivity and decreasing the detection limits, measurements were carried out using multiple square wave

voltammetry, operating in the MSW-DD mode (see Experimental).

Fig. 8 shows the cathodic patterns recorded in MSW-DD at a NCE after equilibration in open circuit in 4×10^{-6} M methylmercury solution, recorded using different ΔE values. The MSW-DD voltammograms are characterised by signals very well resolved from the background. A value at -0.580 V was calculated as the mean value of the maximum and minimum of the peak potentials which is very close to the $E_{1/2}$ value [22]. This value is independent of ΔE . Peak heights measured as the peak to peak amplitude, increase linearly with ΔE , so that the highest sensitivity is obtained for $\Delta E = 100$ mV. The dependence on ΔE obtained for the DD peak height for methylmercury at the NCE agrees with previous literature findings [18,36] obtained by applying MSWV in the normal mode at the HMDE for copper determinations. It should be noted that the increase in ΔE must be limited to a maximum value as, for instance, $n\Delta E = 100$ mV, because of the increasing contribution of the capacitive current and because of the need of applying a potential perturbation within the domain of the electrochemical reaction ($60/n$ mV for a reversible reaction). This clearly appears in Fig. 8 where an increase in ΔE produces more sloping baselines. The insert in Fig. 8 shows that a compromise can be found

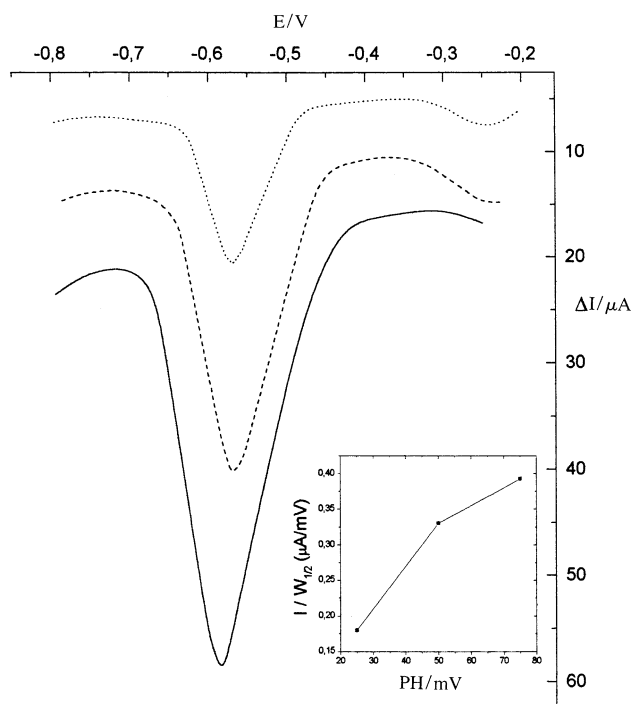


Fig. 7. Osteryoung's square wave voltammograms recorded at a NCE equilibrated in a 2×10^{-5} M $\text{CH}_3\text{HgCl} + 0.01$ M HClO_4 solution at different frequencies: 60 Hz (dotted line); 90 Hz (broken line); 120 Hz (full line). Pulse height: 25 mV. Insert: dependence of the ratio between peak current and peak width at half-height on the pulse height.

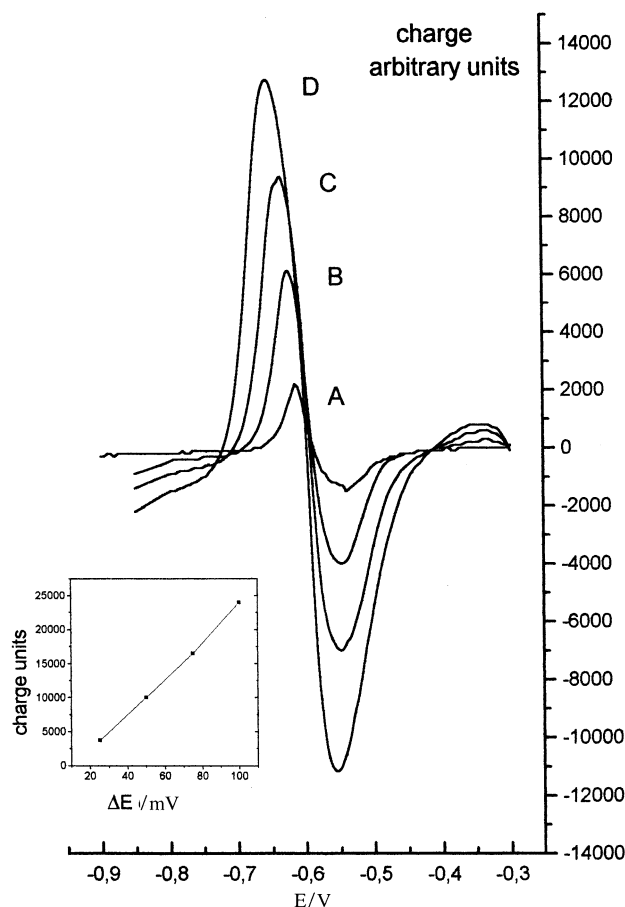


Fig. 8. Direct reduction scans recorded in multiple square wave voltammetry at a NCE in 4×10^{-6} M $\text{CH}_3\text{HgCl} + 0.01$ M HClO_4 . Equilibration time: 15 min in open circuit. ΔE values: (A) 25; (B) 50; (C) 75; (D) 100 mV. Other experimental parameters: $\Delta E_s = 5$ mV, $N = 20$. Insert: dependence of peak heights (peak to peak amplitude in charge units) on ΔE .

to optimise the sensitivity with a good baseline and peak width.

The response of the system with respect to the number N of pulses (periods) per step of the staircase shows a linear increase within an interval from 2 to 128 [18], which is the range of values provided for this instrument. However, since in the prototype instrument 'MPulse' the signal recorded is normalised with respect to the number of pulses, the increase of N is reflected by a better signal to noise ratio, rather than in higher peak signals. This has been verified experimentally for the HMDE [17,18,21,26] and seems to be confirmed also in the present study with modified electrodes. However, it is worth noting that the number of pulses over each step of the staircase increases the time of the measurement, suggesting that also here a compromise should be found. The values of ΔE and N should be chosen carefully for each case. For example, for the analysis of Cd^{2+} at a hanging mercury drop electrode, preliminary tests carried out using the not optimised values of $\Delta E = 50$ mV and $N = 96$, indicated that the

smaller concentration detectable in these conditions was around 10^{-9} M [18]; however, further optimisation of the experimental parameters showed that it was possible to lower the detection limit below 10^{-11} M Cd^{2+} (representing less than 1 ppt) in a sample of KNO_3 Suprapur[®] by using $\Delta E = 35$ mV and $N = 12$ [21]. For the present case of the reduction of methylmercury, the optimisation procedure suggested the use of $\Delta E = 100$ mV and $N = 20$, which resulted in a high sensitivity in front of an acceptable baseline distortion.

Fig. 9 shows the cathodic patterns in MSW–DD recorded at the NCE in 40×10^{-9} M methylmercury solution. The insert shows the calibration plot obtained for measurements carried out in the nM concentration range. The plot is linear with a dynamic range extended at least up to 500 nM (not shown in the insert) and a sensitivity of 2 charge units/nM. Note that because of the different mode of sampling, integrating and combining the rough current transient information, this sensitivity cannot be directly compared to the sensitivity of other usual pulsed techniques in terms of current per mole ($\mu\text{A}/\mu\text{M}$ or equivalent), since the MSW–DD units are different in nature. The detection limits ($\text{DL} = 3 \sigma_b/m$, see above), however, can be significantly compared. The detection limit calculated for MSW–DD

(which is characterised by $\sigma_b = 0.03$ charge units, as determined from five independent blank measurements) gives 4.5×10^{-11} M. This is a DL value significantly lower than detection limits obtained with conventional pulsed techniques. It is worth noting that this is a calculated DL value. Measurements at concentrations in close proximity to this limit were not performed in this work, because of problems in avoiding sample contamination at such low concentration levels. However, the characteristics of data obtained in the nanomolar range support the applicability of the method, at least in the concentration range shown in Fig. 9.

4. Conclusions

Nafion[®] coated glassy carbon electrodes can be successfully used for preconcentrating and determining trace methylmercury. The performances achieved with the modified electrode can be further improved by using conventional pulsed techniques (such as differential pulse or Osteryoung's square wave voltammetry), and even further enhanced by using an advanced multiple pulsed method recently developed, such as multiple square wave voltammetry.

This work is the first report of an application of multiple square wave voltammetry to solid modified electrodes. The ability of MSWV and of its double differential mode, MSW–DD, to enhance strongly the signal to noise ratio, which was previously demonstrated for mercury electrodes, especially in anodic stripping voltammetry, is found to be operative even with solid modified electrodes in the direct reduction mode.

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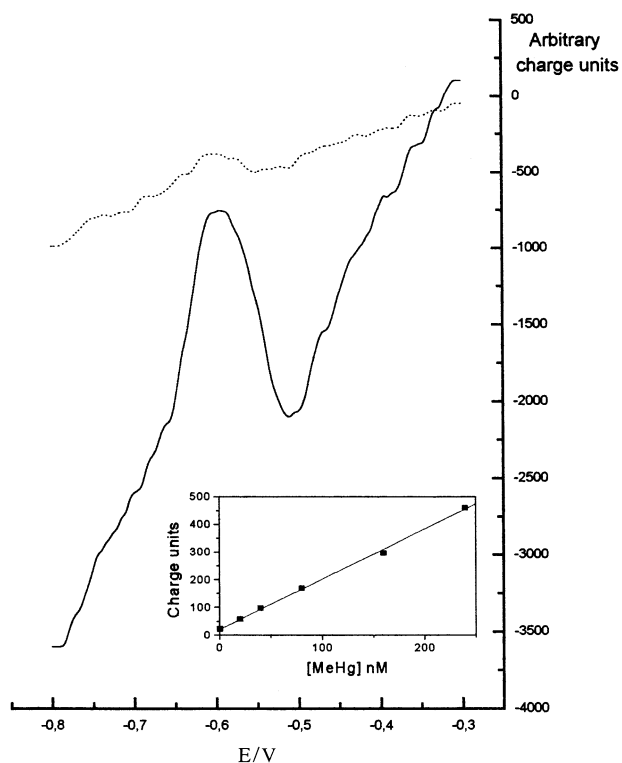


Fig. 9. Multiple square wave voltammograms (reduction scans) recorded at a NCE in 0.01 M HClO_4 blank solution (dotted line) and after spiking with 40×10^{-9} M CH_3HgCl (full line). Experimental parameters: $\Delta E_s = 5$ mV, $\Delta E = 100$ mV, $N = 20$, equilibration time = 15 min in open circuit. Insert: calibration plot for increasing additions of CH_3HgCl .

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