Multi-electrode detection in voltammetry Part 3.† Effects of array configuration on the Hadamard multiplexed voltammetric technique

The Analyst

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The effect of the number of electrodes and their relative distribution on the gain of the signal-to-noise ratio (SNR) in a multiplexed voltammetric measurement was evaluated. A voltammetric multi-channel instrument was constructed capable of operating with up to 63 ultramicroelectrodes (mercury coated copper discs , diameter 55 μm). The gain in the SNR was investigated as a function of the number of electrodes (15, 31 and 63) in the array. For each array a design matrix was employed for the multiplexed measurements. The results show that the detection limit for Pb(II) can be improved 5.1-fold by employing 63 electrodes. The overlapping effect of diffusion layers was also evaluated and the results allow the conclusion that, for multiplexed readings obtained at 100 per second, and when the distance between adjacent electrodes is less than 20 times their diameter, the radial component is disturbed, causing a reduction in the faradaic current. On the other hand, by keeping the distance greater than this limit, the multiplex gain can be fully achieved with a substantial reduction in data acquisition time.

Introduction

The use of ultramicroelectrodes (UMEs) in electrochemistry and electroanalytical chemistry has become of great interest owing to their outstanding electrochemical behaviour, arising from their ultra-small dimensions (on the scale of micrometres), which are of the same order of magnitude as the diffusion layer.[1–7] Recently, the field for UMEs has been significantly broadened with applications extended to areas such as bio-electrochemistry, surface electrochemistry and neurotransmitter and enviromental pollution monitoring.[1–10] Detailed descriptions of the advantages and disadvantages of the use of such electrodes can be found elsewhere.[1–11]

One of the difficulties found when UMEs are employed arises from the small current values generated. The problem can be approached by using arrays of interconnected UMEs for which the sum of individual currents can be monitored. The use of UME arrays has received special attention because the intrinsic properties of the electrodes are preserved in the array and some advantages can be obtained. Among these are miniaturisation of the electroanalytical cell (including easy employment in flow systems), increased signal-to-noise ratio (SNR),[12–16] use of interdigitised arrays where the potential of one array is set to produce an electrochemical species detected by the other array[17–19] and the possibility of individual access to each of the electrodes taking part in the array, ensuring that selective signals for electroactive analytes can be obtained in view of the potential applied to different electrodes or by chemical modification of their surfaces.[20]

Advances in the construction of arrays of UMEs have not been fully exploited and only the three first characteristics listed above are fully described in the literature, and only a few studies have dealt with the aspects of individual access to the UMEs in the array.[20–23] Full achievement of the advantages present in UME arrays is strongly dependent on the development of multi-channel instruments.[24,25]

Arrays of UMEs show peculiarities in relation to the behaviour of the diffusion layer between two neighbouring electrodes. When the excitation potential is applied in a voltammetric measurement, each UME will show an independent behaviour. Some time later, the radial component of the diffusion layer will become important and of the same magnitude expected for a single UME. However, for a long time interval after potential application, there is an overlapping of the diffusion layers of adjacent electrodes and a consequent decrease in the concentration of the electroactive species in the vicinity of the electrodes.[26] Therefore, during the first instants of potential application, the current follows a planar model, considering only the active surfaces of the UMEs, whereas for long time intervals, the current follows the same model but for the whole surface (active and inactive) of the electrodes. For intermediate time intervals the behaviour is like that predicted by a spherical model and the time necessary for the change from a planar to a spherical model is determined by the distance between two adjacent electrodes.[27] Previous investigations revealed that the minimum distance between two adjacent electrodes in a array should be greater than six times their diameter to avoid overlapping of the diffusion layers when the scan rate is lower than 20 mV s^{-1}.[12,27]

The specific behaviour of UMEs should be taken into account in array construction in order to optimise its characteristics, mainly when the Hadamard multiplexing technique is to be employed.[25]

As described previously,[25] the multiplexed Hadamard voltammetric technique allows for a increase in the SNR, keeping the time necessary for data acquisition ideally the same as in a non-multiplexed acquisition. When the Hadamard technique was first employed for voltammetric measurements some particular characteristics were observed. During the acquisition, the multiplexed currents of the electrodes belonging to an array are submitted to pulses of potential applied following each row

† For Part 2 see ref. 25.

of the Hadamard design matrix.[25] Therefore, it was observed that the chemical environment around an electrode changes during the multiplexed measurements and, if the scan of the matrix rows is performed at once, some distortions are observed in the recovered voltammogram. In order to minimise this effect, a dummy pre-scan and a resting time interval between the multiplexed readings were employed.[25] This artifice results in an undesireable increase in the time interval necessary for acquisition of the multiplexed data, reducing the multiplexing gain.

In this work, the multiplexed voltammetric technique was investigated with the aid of an improved instrument which can access up to 63 independent electrodes in a array. A detailed study of the overlapping of the diffusion layers between adjacent electrodes and its effect on the multiplexing gain is described.

Experimental

Multi-channel voltammetric instrument

The voltammetric instrument employed is similar to that described previously.[24] However, the new instrument is capable of operating with up to 63 electrodes. New software, written in Visual Basic 3.0, was developed to perform the same functions as described previously.[24,25]

Electrode array

An array made of 63 individual copper wires (55 μm diameter), covered with metallic mercury and arranged in a circular format, was constructed. Electrical isolation and mechanical stability of the array were achieved by encasing the array in a polyester resin placed in a cylindrical mould and cured for 24 h. The electrode array preconditioning operations and mercury film deposition procedure were described in Part 1.[24] The distances between adjacent electrodes in the array were set to 10 times their diameter.

Defining sub-arrays of electrodes

Owing the versatility of the instrument and associated software, it was possible to define different sub-arrays from the total of 63 UMEs of the array. For each sub-array a Hadamard matrix was employed for multiplexed data acquisition.[25]

The sub-arrays were defined to contain 15 or 31 electrodes arranged in different modes with the aim of investigating the effect of distance between adjacent electrodes on the overlapping of the diffusion layers. Sub-arrays containing 31 electrodes were employed in multiplexing readings with the adjacent electrodes 550 or 1100 μm apart. This is easy to do in this instrument by either accessing immediately adjacent electrodes or by jumping one electrode. For arrays of 15 electrodes, the effect of overlapping could be investigated for the same distances and also for 2200 μm (accessing one electrode and jumping three adjacent electrodes).

Fig. 1 shows how the distances among electrodes in a sub-array are managed and the expected behaviour of the diffusion layer as the distance between adjacent electrodes is increased.

The results of the effect of the distance among electrodes on the overlapping of the diffusion layer for the multiplexed technique were always obtained by employing 100 multiplexed readings per second.

Reagent and solutions

All solutions and reagents were as described previously.[24]

Results and discussion

In a multiplexed scan of an electrode array it is necessary that the current produced by each electrode is the same every time an electrode is included in a measurement. Pseudo voltammograms obtained after data treatment of the multiplexed readings were shown in Part II.[25] To overcome this problem, any multiplexed scan of an array of UMEs was made after a false scan. However, a small fraction of these distortions was still observed. Employing a resting time interval, with a potential applied to the electrodes capable of stripping the reduced metal, eliminated the distortions observed in the recovered pseudo-voltammogram.[25] However, the time necessary to acquire the multiplexed data increased by a factor of four, lowering the multiplex gain.

It was observed that the presence of traces of dissolved oxygen was one of the factors responsible for causing the distortions observed previously.[25] Fig. 2 shows some pseudo-voltammograms for Pb(II) obtained with the Hadamard protocol with and without dissolved oxygen present. In its presence, the first multiplexed scan produces a large distortion in the pseudo-voltammogram whereas in the absence of the dissolved gas no distortion is observed. This behaviour can be explained by considering that oxygen undergoes an irreversible reaction at

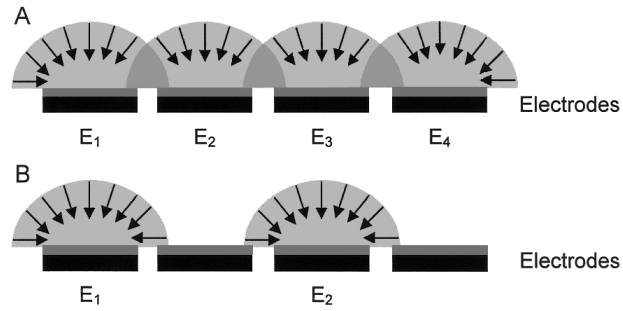

Fig. 1 Effect of distance between electrodes in a sub-array on the difusion layer. (A) 550 and (B) 1100 μm.

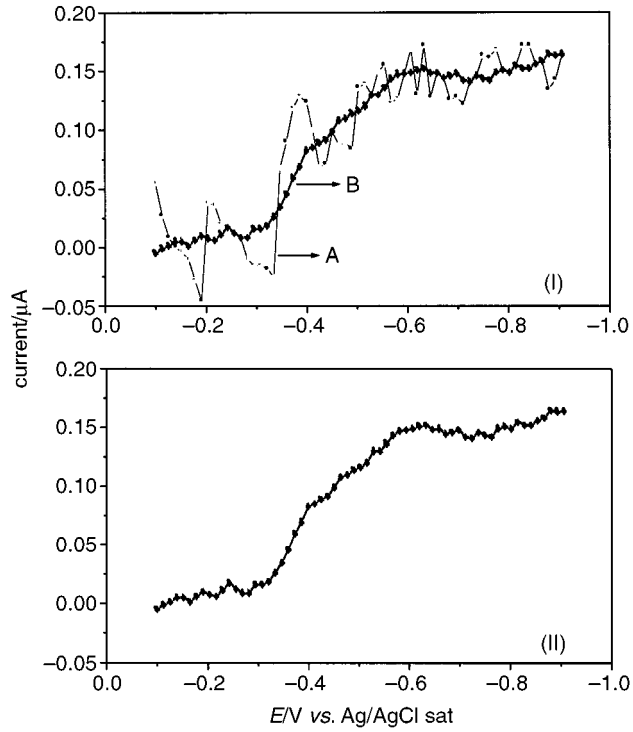

Fig. 2 Pseudo-voltammetric curves obtained for the multiplexed technique: (I) with dissolved oxygen, first (A) and second to fourth (B) multiplexed scans; (II) four (superimposed) scans after complete removal of dissolved oxygen. 0.5 mmol L^{-1} Pb(II) in 0.1 mol L^{-1} $NaNO_3$.

potentials near −0.05 V. Therefore, during the first multiplexed scan, the current in each electrode is the sum of that produced by the reduction of the metal and that produced by the oxygen. The concentration of oxygen is altered on the surface of the electrodes during the successive multiplexed readings. As the oxygen reaction is not reversible, the effect of the resting time interval is not observed, because its initial concentration cannot be re-established. Furthermore, the diffusion process is also not capable of re-establishing the concentration of gas at the scan rate employed.

The considerations above suggested that, for multiplexed measurements involving irreversible electrochemical systems, the minimum time interval necessary between the multiplexing reading will be limited by the diffusion of the electroactive species. In this case, the use of electrodes of smaller dimensions would improve the mass transport to the electrode surface. The steady state would be reached faster and the time interval between measurements could be shortened, approximating the predicted theoretical value.[12]

The first consequence of the identification of the dissolved oxygen effect was to reduce the time interval necessary for multiplexed data acquisition, achieved by purging the electrochemical cell with high quality nitrogen. However, even in the absence of dissolved oxygen, attempts to employ higher scan rates resulted in distortions, because insufficient time was given to re-establish the diffusion layer. Hence the adoption of a resting time interval that allows the re-dissolution of the electroactive species was still necessary when the multiplexed readings are taken at high scan rates (> 1000 mV s^{-1}). It was observed that, for a scan rate of 1000 mV s^{-1}, a resting time of 1 ms between each multiplexed reading is sufficient to ensure the absence of distortion in the pseudo-voltammogram. On the other hand, current values equal to those observed for the conventional array scan were obtained only when this time interval was 10 ms. This time interval is about 10 times lower than that employed previously,[25] permitting data acquisition to be three times faster.

Signal-to-noise improvement and number of electrodes in the array

Fig. 3 depicts the pseudo-voltammetric curves obtained by the electrode scan and Hadamard multiplexed techniques. For both techniques it is possible to observe differences among the surface areas of the electrodes in the array.[25] Employing the data shown in Fig. 3, the correlation between the faradaic current (i, nA) and the Pb(II) concentration [$C_{Pb(II)}$ μmol L^{-1}] was established as $i = 0.1783 (\pm 0.001) C_{Pb(II)} + 0.6 (\pm 0.4)$ and $i = 0.1896 (\pm 0.001) C_{Pb(II)} + 0.6 (\pm 0.3)$, both with correlation coefficients of 0.9999, for the electrode scan and for the multiplexed technique, respectively. Both techniques showed a similar behaviour for this relationship. However, the multiplexed technique, as shown in Table 1, presents a lower detection limit for Pb(II) than the electrode scan technique.

The lower detection limit obtained for the multiplexed technique is a consequence of the improvement in the SNR of the current measurements. As described previously,[25] the multiplexing made by using the Hadamard transform will cause an improvement in the SNR of the measurements as a function of the number of multiplexed electrodes.

The effect of the number of electrodes employed in a multiplexed scan was evaluated by observing arrays containing 15, 31 and 63 electrodes and employing Pb(II) solutions in the range 25–600 μmol L^{-1}. The results are summarised in Table 2, where it is possible to observe the improvement in the detection limit and in the scan rate as the number of electrodes in the array is increased. For comparison purposes, the detection limit for the non-multiplexed electrode scan technique was found to be 200 μmol L^{-1}. This value is constant and independent of the number of electrodes employed in the array.

The gain in the scan rate achieved for the multiplexed technique was found from the ratio between the time interval necessary to perform m measurements using the electrode scan technique, where m is the number of times the electrodes are employed in the multiplexed measurement. This means that m reflects the number of times a electrode must be measured for the mean current produced by it to become statistically equivalent to the value found by the multiplexed technique.

The theoretical gain in the SNR predicted for the Hadamard multiplexing technique is equal to $N^{1/2}/2$, where N is the number elements taking part in the multiplexed measurement. Therefore, the expected gain for 15, 31 and 63 electrodes should be

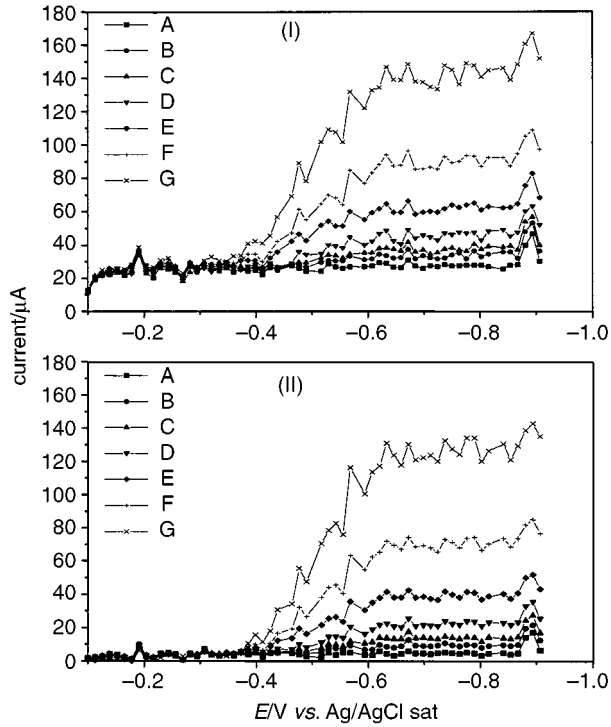

Fig. 3 Pseudo-voltammetric curves obtained by the multiplexed technique showing the behaviour of the faradaic current as function of the concentration of lead in 0.1 mol L^{-1} $NaNO_3$ solution [A, blank; B–G, 24, 48, 95, 186, 358, 666 μmol L^{-1} Pb(II), respectively]. Pseudo-voltammetric curves obtained by (I) electrode scan and (II) multiplexed scan.

Table 1 Comparison of the detection limit (DL), ratio of detection limit (RDL) and gain in acquisition time (GAT) for the multiplexed scan (MS) and electrode scan (ES) techniques

No. of electrodes in the multiplexed scan	DL/ μmol L^{-1}	RDL (ES/MS)	GAT (t_{ES}/t_{MS})
15	92	2.2	6
31	53	3.8	12
63	39	5.1	24

Table 2 Detection limit (DL) for Pb(II) as a function of the distance between two adjacent electrodes for a multiplexed scan employing 15 electrodes

Distance between electrodes/μm	DL/ μmol L^{-1}
550	92
1100	57
1650	53
2200	48

1.9, 2.8 and 4.0, respectively. A full multiplexing gain would be obtained when the predicted gain in the SNR is achieved in the same time interval necessary for a non-multiplexed measurement.[25] Table 1 shows that the gain in the SNR is slightly higher than predicted. This can be explained by the differences in the way the potential pulse is applied in the multiplexed and non-multiplexed scans. On the other hand, despite the improvement achieved in the SNR, the full gain in the data acquisition time was 25% lower than predicted, although still three times better than described previously.[25] The cause of this is the 10 ms resting time interval employed between successive multiplexed measurements.

Overlapping of the diffusion layers

Table 2 gives the values of the detection limits for Pb(II) as a function of the distance between adjacent electrodes employed in the multiplexed scan. The electrode scan technique did not show any alteration in the detection limit as a function of the electrode distance. Therefore, only one value is presented in Table 2.

The faradaic current increases with distance and this allows the conclusion that, for distances shorter than 1100 μm (20 times the electrode diameter) there is a deterioration of the detection limit. The results show an overlapping between adjacent diffusion layers for distances shorter than 1100 μm or, at least, a perturbation of these layers. The effect can be related to a decrease in the component responsible for the radial mass transport, which could be affected by overlapping. The overall effect causes a decrease in the faradaic current at lower detection limits for Pb(II).

Conclusion

The multiplexed technique applied to arrays of UMEs showed a significant increase in the SNR for voltammetric measurements when compared with a conventional electrode scan, confirming the results reported previously.[25] The detection limit for Pb(II) using the electrode scan method was 200 μmol L^{-1}, whereas for the multiplexed approach it was 92, 53 and 39 μmol L^{-1} using 15, 31 and 63 electrodes, respectively. In addition, it was possible to conclude that the number of electrodes employed in the array, when a multiplexed reading is employed, improves the detection limit as predicted by theory.

One of the causes of the distortions observed in the pseudo-voltammograms obtained previously,[25] using multiplexed measurements, was the presence of oxygen. The effective removal of this species made it possible not to use the pre-scan procedure employed previously. However, it was confirmed that a resting time between multiplexed readings is still necessary and this indicates that a full multiplexing gain can be achieved only with the use of electrodes of even smaller dimensions principally for irreversible electrochemical systems.

The results of the effect of the distance between electrodes using the multiplexed approach revealed that the detection limit is improved with this distance. Thus, when the distance is increased from 550 to 2200 μm, the detection limits for Pb(II) were 92 and 48 μmol L^{-1}, respectively. These results show that the multiplexed measurements are affected by the overlapping of adjacent diffusion layers. For electrodes of the dimensions reported in this work it is recommended that, for use in multiplexed techniques at a reading ratio of 100 per second, the distance between adjacent electrodes is, at least, 20 times their diameters.

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