The Analyst

Multi-electrode detection in voltammetry

Part 2.† Evaluation of a Hadamard multiplexed voltammetric technique

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A multiplex approach has been evaluated to obtain individual voltammetric signals coming from an array of independent microelectrodes. The multiplex design employs *S* matrices and the Hadamard transform to recover the signals for each electrode. Two pulse like voltammetric techniques, resembling the conventional normal pulse and differential pulse techniques, have been employed to generate the multiplexed currents. An array of 31 microelectrodes has been employed and the signal-to-noise ratio (S/N) obtained for the measurements presented a gain that is close to the 2.78 value predicted by the multiplex design. However, the reduction in the time interval spent for data acquisition was not 16, as predicted but 3 times. The increase in the data acquisition time for the multiplexed reading is a consequence of the pulse techniques employed. These techniques cause depletion of the electroactive specimen near the electrode surface. To overcome this problem a resting potential of 100 ms and a false multiplexed pre-scan must be employed. The gain in the S/N obtained allows for a three times enhancement in the detection limit for Pb^{II} determination when compared to the same non-multiplexed technique.

Current requirement for high versatility and speed in data acquisition by voltammetric techniques has induced the use of arrays of ultramicroelectrodes (UMEs) that can be accessed in groups or individually.[1–8] Specially constructed instruments have been described in the literature to permit a multichannel approach to voltammetry.[9–14] In such approaches, each electrode is taken as an individual sensor and scan procedures are used to obtain the faradaic current generated by each electrode. However, the instruments and data acquisition procedures described thus far take the individual current of each electrode in a sequential procedure.

The use of UMEs has some well known advantages over electrodes of conventional size.[15,16] However, while in a voltammetric technique employing UME a higher density of current is obtained the absolute values of the currents are smaller than those obtained by electrodes of conventional size.[17] This means that most of the gain obtained by working with microelectrodes can be jeopardised, concerning their analytical use, by the poor signal-to-noise ratios (S/N) found in the measurements. Therefore, improved and more expensive electronics become necessary and the average of a large number of measurements for each electrode are frequently employed in order to improve the S/N.[18] The delay imposed on a data acquisition procedure, caused by employing the average of sequential scans of the array, could be intolerable when, for example, the array is being used in flow analysis or as an HPLC detector.

Up to the present moment, there is no work reporting on Hadamard multiplexing techniques to improve the S/N in electrode array multichannel voltammetry. Multiplexed reading techniques have the advantage of keeping the time interval necessary to average a number of measurements ideally the same as that necessary for only one scan over the elements to be measured. The Hadamard multiplexing technique, for example, has frequently been applied to enhance the S/N of measurements in spectral data acquisition.[19]

The voltammetric multichannel instrument, described in Part 1,[20] has the necessary characteristics to allow the Hadamard multiplexing data acquisition procedure to be applied for the first time in voltammetric measurements of electrode arrays. The instrument has been constructed to work with up to 31 microelectrodes ($[2^k - 1]$ electrodes, $k = 5$). This number of elements is necessary to use the Hadamard approach to multiplex reading of the faradaic current. This work has the objective of investigating the effect of the Hadamard multiplexing technique on the S/N of simple voltammetric multichannel techniques that employ arrays of microelectrodes.

Theory

Hadamard multiplexed voltammetric reading of electrodes arrays

To perform a multiplexed current reading from an electrode array the multichannel instrument must be capable of accessing signals that are combinations of individual currents produced by some of the electrodes. The number and the selected electrodes whose signal should be combined to produce a multiplexed reading are defined by the multiplexing strategy employed. One of the most common and efficient ways to multiplex measurements, widely employed in spectrophotometry,[21] is the Hadamard transform method.

The Hadamard multiplexing method requires the use of $2^k - 1$ elements from which any signal is intended to be extracted with improved S/N. Fig. 1 shows an example that compares the way a measurement could be obtained for an array of three electrodes ($k = 2$). In the conventional way, the current generated for each electrode under the applied excitation potential is acquired sequentially and individually [Fig. 1(A)].

Noise associated with the measurement (including electronic noise from the transducer) is present in all of the three current

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† For Part 1, see ref. 20.

values obtained. The multiplexed measurement also requires three readings as described in Fig. 1(B). However, two signals produced by two selected electrodes are always added. The three measurements obtained contain the same amount of noise present in each of the conventional individual measurements. And, of course, the measurements obtained need to be demultiplexed by some mathematical treatment to recover the original signal associated with each electrode.

The characteristics of the total noise and the relative contribution of its components will determine the effectiveness of the multiplexed reading to improve the S/N of the measurements. For spectrophotometric measurements, white noise usually associated with the detector, predominates and the multiplexing strategy is effective. Apparently, multiplexing is not effective in reducing shot and pink noise in spectrophotometric measurements.[21] However, for an electrochemical voltammetric measurement, characterisation of the noise is somewhat more difficult. For a start, the distinction between detector and source is not as clear as in spectrophotometric experiments. The gain in S/N for a multiplexed voltammetric reading, will be possible only if the noise imposed by additional electronic circuitry, required for the multiplexed reading do not increase the total noise amplitude beyond the gain in S/N that could, in theory, be predicted by the multiplexing design.

Despite the difficulty to establish if that noise amplitude increase will occur or not, a comparison of the S/N obtained in a non-multiplexed with that obtained in a multiplexed reading is an empirical and effective way to ensure the electrochemical measurement can take advantage of multiplexing.

Signal recoverering

When the Hadamard approach is employed in a multiplexed data acquisition system the recovery of individual signals requires very simple mathematics. For systems resembling the single pan balance model, the ***S*** matrix, derived from the Hadamard matrix, gives the best multiplex gain.[21] A multichannel instrument in which an electrode can only be or not be included in a measurement, under control of the operator, must employ the single pan model and the ***S*** matrix. The ***S*** matrix does contain 0 and 1 elements that are associated, respectively, to an unconnected and to a connected electrode in a multichannel multiplexed reading. The matrix column ***y*** of the signals can be obtained, for a ***S*** matrix by:

$$\boldsymbol{y} = \boldsymbol{S}^{-1}.\boldsymbol{M} \qquad (1)$$

where ***M*** is the matrix column of the multiplexed measurements. The inverse of the matrix ***S*** ($\boldsymbol{S}^{-1}$) can be obtained by the equation:

$$\boldsymbol{S}^{-1} = 2/k + 1.\boldsymbol{Q} \qquad (2)$$

where ***Q*** is a matrix obtained by replacing each zero of the ***S*** matrix by -1, keeping the 1s originally present. Therefore, the Hadamard transform operation which enables recovering the original non-multiplexed signals employs basically additions and subtractions and can be performed by the use of low cost microcomputers. The predicted gain in the S/N for signals recovered from a multiplexed reading made by using the ***S*** matrix is ($1/2.k^{1/2}$), where k is the number of multiplexed elements or, in the present case, the number of independent electrodes in the array.

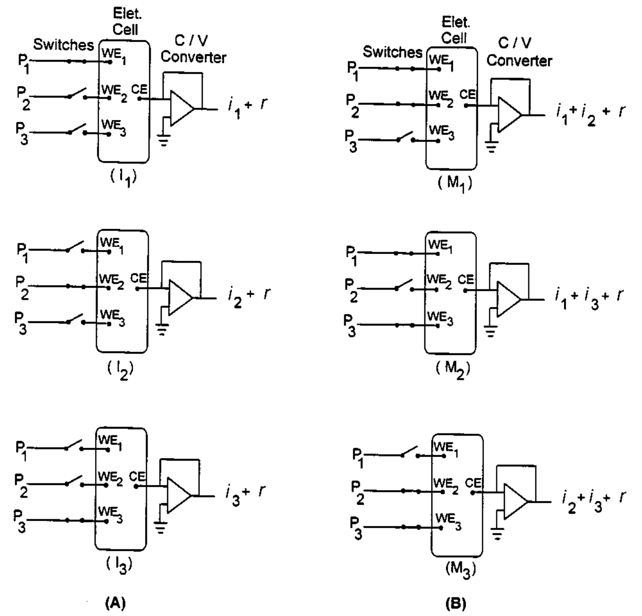

Fig. 1 Schematic diagram showing the difference between (A), a conventional non-multiplexed voltammetric data acquisition from an hypothetical array containing three working electrodes in a two electrode electrochemical cell model; and (B), a multiplexed data acquisition with the same array. P_{1-3}, potential applied to each electrode; WE_{1-3}, working electrodes; CE, counter electrode; i_{1-3}, current associated with each electrode, r, noise associated with each measurement; I_{1-3} and M_{1-3}, conventional and multiplexed measurements, respectively.

Experimental

The multichannel voltammetric instrument and the electrode array of 31 electrodes ($2^k - 1$, $k = 5$) described in Part 1[20] have been employed to evaluate a multiplexed reading procedure for two voltammetric techniques. The hardware of the instrument allows connecting any of the 31 electrodes in any order to obtain a multiplexed reading that is equal to the sum of the individual currents produced by the electrodes. The selection of the electrodes employed in a multiplexed reading was made by sending control bytes to four ‘latches’ integrated circuits. Each digital output of these integrated circuit controls the analog switch that connects the electrode to the voltammetric cell. The patterns of bits sent to the latches were stored in variables reproducing sequentially each of the lines of ***S*** matrices employed for the multiplex design. Fig. 2 shows the two ***S*** matrices employed in this work. The first one is named ‘normalised matrix’ and the second is termed ‘cyclic matrix’. The way such matrices can be obtained has been described elsewhere.[22,23]

Fig. 3 shows a flow chart containing the main operations effected, under computer control, to obtain a set of voltammetric signals from a multiplexed array reading procedure. The initial and final potential are applied to the array by the two digital-to-analog devices present in the instrument and the 31 multiplexed reading are obtained. In another procedure, a constant small amplitude pulse (50 mV) is imposed over the previously established potential for each electrode. Differential multiplexed measurements are obtained by subtracting the current reading after from the one read before pulse application. The resulting pseudo voltammetric curve resembles that obtained for the conventional differential pulse technique.

Array of microelectrodes

The array of mercury film copper microelectrodes described in Part 1[20] has been used thoroughout.

Reagent and solutions

All solutions employed are as described in Part 1.[20]

Results and discussion

The first attempts to apply the multiplexed technique to obtain the individual currents associated with each electrode resulted in signals showing an unexpected profile. The expected sigmoidal profile that should be composed by the individual currents of successive electrodes was hardly distinguishable, as shown in Fig. 4(A). As pointed out in Part 1,[20] the currents associated with each electrode are additive. Therefore the lack of additivity can not be taken as the limiting factor producing the observed distortion in the voltammograms. Furthermore, care was taken to keep the multiplexed currents within the operating range of the instrument. Another factor that could affect the multiplexed measurement is the non-reproducibility of the current associated with each electrode in the successive multiplexed readings in which the electrode takes part. As matter of fact, when the potential applied to the electrode exceeds the value enough to cause reduction of the electroactive specimen, the first time the electrode is connected will produce a current that is higher than the second time. It occurs if the time interval elapsed between two successive readings is not long enough to restore the original concentration of the electroactive specimen at the electrode surface. The effect of superposition of diffusion layers between adjacent electrodes was discharged because the minimum distance among the elements is greater than that recommended to avoid this effect.[1]

Multiplexed Reading	ELECTRODE																														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
1	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1	1	0	1	0	1
2	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1
3	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0
4	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1
5	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0
6	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0
7	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1
8	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1
9	1	0	1	0	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1	0	1	0	1	1	0	1	0	1	0	1	0
10	0	1	1	0	0	1	1	1	1	0	0	1	1	0	0	0	0	1	1	0	0	1	1	1	1	0	0	1	1	0	0
11	1	1	0	0	1	1	0	1	0	0	1	1	0	0	1	0	1	1	0	0	1	1	0	1	0	0	1	1	0	0	1
12	0	0	0	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	0	0	0	0
13	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1	0	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1
14	0	1	1	1	1	0	0	1	1	0	0	0	0	1	1	0	0	1	1	1	1	0	0	1	1	0	0	0	0	1	1
15	1	1	0	1	0	0	1	1	0	0	1	0	1	1	0	0	1	1	0	1	0	0	1	1	0	0	1	0	1	1	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
17	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0
18	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0
19	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1
20	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1	1	1	1	1	0	0	0	0	1	1	1	1	0	0	0	0
21	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1	1	0	1	0	0	1	0	1
22	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0	1	1	0	0	0	0	1	1	1	1	0	0	0	0	1	1
23	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1	1	0	0	1	0	1	1	0	1	0	0	1	0	1	1	0
24	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0
25	1	0	1	0	1	0	1	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	0	1	0	1	0	1	0	1
26	0	1	1	0	0	1	1	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	0	0	1	1	0	0	1	1
27	1	1	0	0	1	1	0	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	0	1	1	0	0	1	1	0
28	0	0	0	1	1	1	1	1	1	1	1	0	0	0	0	1	1	1	1	0	0	0	0	0	0	0	0	1	1	1	1
29	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1	1	0	1	0	0	1	0	1	0	1	0	1	1	0	1	0
30	0	1	1	1	1	0	0	1	1	0	0	0	0	1	1	1	1	0	0	0	0	1	1	0	0	1	1	1	1	0	0
31	1	1	0	1	0	0	1	1	0	0	1	0	1	1	0	1	0	0	1	0	1	1	0	0	1	1	0	1	0	0	1
	V_0															V															V_f

Multiplexed Reading	ELECTRODE																														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
1	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0
2	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1
3	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1
4	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1
5	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1
6	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1
7	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0
8	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0
9	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1
10	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1
11	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0
12	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1
13	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	0	1
14	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0
15	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1
16	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0
17	0	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0
18	0	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	1	1	0	0	0
19	1	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0
20	0	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1
21	1	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0
22	0	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1
23	1	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0
24	1	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1
25	1	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1
26	0	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1
27	1	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0
28	1	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1
29	0	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1
30	0	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0
31	0	1	1	1	1	1	0	0	1	1	0	1	0	0	1	0	0	0	0	1	0	1	0	1	1	1	0	1	1	0	0
	V_0															V															V_f

Fig. 2 Normalised (upper) and cyclic (lower) ***S*** matrices employed in multiplexed data acquisition. In each matrix line, a 1 means that the respective electrode will be connected at the moment of the multiplexed current reading. V_0, initial potential (applied on the first electrode of the array) and V_f, final potential (applied on the last electrode of the array).

At this point, the normalised ***S*** matrix has been employed in multiplexed data acquisition. As the effect of the depletion of the electroactive specimen at the electrode surface has been observed to be important in the multiplexed reading, the cyclic matrix was also investigated as an alternative for the multiplex design. The cyclic matrix provides, for each matrix line, a different distribution of electrodes employed in the data acquisition. In the cyclic matrix, the electrodes are more randomly distributed in the lines of the matrix than in the normalised matrix. Also, when compared with the normalised matrix, the cyclic one allows the employment of all 31 electrodes of the array at least once before the 5th line of the matrix is achieved. On the other hand, the normalised matrix can only achieve this goal on the 16th line. Fig. 4(B) shows the pseudo voltammetric curves obtained after only one multiplexed scan employing the cyclic matrix. The behaviour of the voltammetric signals is still far from the expected one but, at least, the final electrodes of the array show the expected higher values for the faradaic current.

A false initial multiplexed scan was performed to try to equal the current response for each electrode during successive multiplexed readings. This false pre-scan is made exactly as the multiplexed scan described in Fig. 3 but the acquired current data are discharged. Fig. 4(C) shows that, after a pre-scan, the

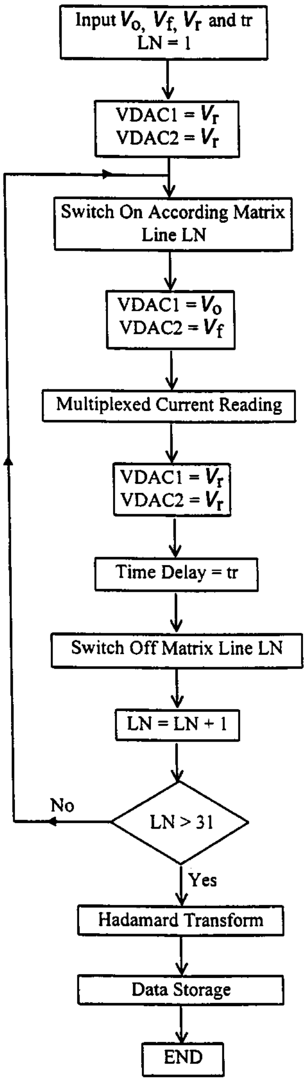

Fig. 3 Flow chart showing the computer controlled steps necessary for a normal pulse multiplexed data acquisition from the array of 31 microelectrodes. V_0, initial potential; V_f, final potential; V_r, resting potential; LN, line number of the normalised or cyclic ***S*** matrix; VDAC1 and VDAC2, output voltage of the digital-to-analog converters 1 and 2, respectively; tr, resting time interval.

current values showed the expected behaviour. One the other hand, because the simulated scan causes depletion of the electroactive specimen, reducing its concentration around the electrode, the limit current generated in the second multiplexed scan is about half of that obtained in the electrode non-multiplexed scan technique described in Part 1.[20] In order to restore the concentration of the electroactive specimen around the electrodes the effect of a short resting time interval between successive multiplexed readings was investigated. Fig. 5 shows that, if a resting time interval of about 100 ms is employed between readings, the current values obtained after demultiplexing is about the same as those obtained for the electrode scan technique. The pseudo-curves have been smoothed by using moving average applied to the current signals for better visualisation of data.

The procedure adopted to obtain the data reported below included a pre-scan and a resting time interval of 100 ms between readings. The cyclic matrix has been employed in all measurements. The adoption of this procedure imparted a reduction of the equivalent potential scan rate and resulted in a time interval necessary for data acquisition that is about five times longer than the one necessary to acquire the non-multiplexed data. However, if an equivalent 16 non-multiplexed readings need to be performed to enhance the S/N of the measurement, it will take a time interval that is three times longer than necessary for the multiplexed reading. Therefore, a real multiplex gain is obtained in terms of time interval necessary to achieve the same S/N.

The behaviour of the current as a function of concentration and the effect of multiplexing on detection limit is of major interest in order to apply such procedures to analytical determinations. Fig. 6 shows some pseudo voltammetric curves obtained after transforming the multiplexed measurements for solutions containing variable concentrations of Pb^{II}. In Fig. 6(I), the normal pulse technique has been applied while Fig. 6(II) shows results for the differential pulse technique. The pseudo voltammetric curves show very good characteristics and demonstrate that the multiplex approach is capable of recovering the individual signals for each electrode. Statistical parameters for analytical curves can be observed in Table 1.

The relative standard deviations for six measurements of the limit current for a 0.1 mmol l^{-1} Pb^{II} solution is equal to ±0.2% and ±0.4% for the normal and differential pulse, respectively. These values are about three times lower than those observed for multichannel non-multiplexed equivalent methods.

The detection limits (DL) for Pb^{II} were found to be equal to 4 and 12 μmol l^{-1}, respectively, for the normal and differential pulse multiplexed methods. In Part 1 is described the reason why, for a multichannel voltammetric technique, the DL for differential pulse is worse than that in normal pulse. Both techniques show a standard deviation for the residual current that is at least two or three times lower than the values found for the equivalent non-multiplexed techniques. The experimental gain obtained in the S/N, after analysis of the data reported above, is close to the 2.78 value expected on the basis of the multiplexing theory employing ***S*** matrices.[19]

To confirm the gain obtained in the S/N for the multiplexed voltammetric technique, the shielding, usually employed around the electrochemical cell, was removed and the residual current for a 0.1 mol l^{-1} NaNO$_3$ solution was obtained by various techniques. The ambient interference becomes, in the absence of the electronic shielding, the higher component of the noise associated with the current measurements. Fig. 7 shows the magnitude of the noise for the individual residual current of each electrode of the array. The reduction in the standard deviation obtained by the multiplexed measurement can be clearly observed. Also, in this case, the gain approximates the

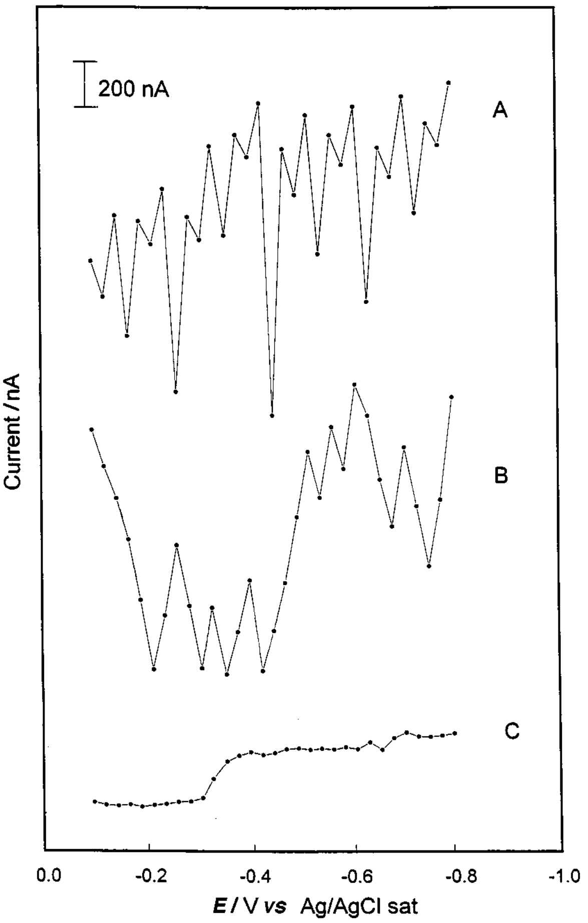

Fig. 4 Pseudo voltammetric curves obtained after Hadamard transform of the multiplexed currents: A, using the normalised matrix; B, using the cyclic matrix; and C, using the cyclic matrix after a first false scan preceding real data acquisition; 0.5 mmol l^{-1} Pb^{II} in 0.1 mol l^{-1} NaNO$_3$.

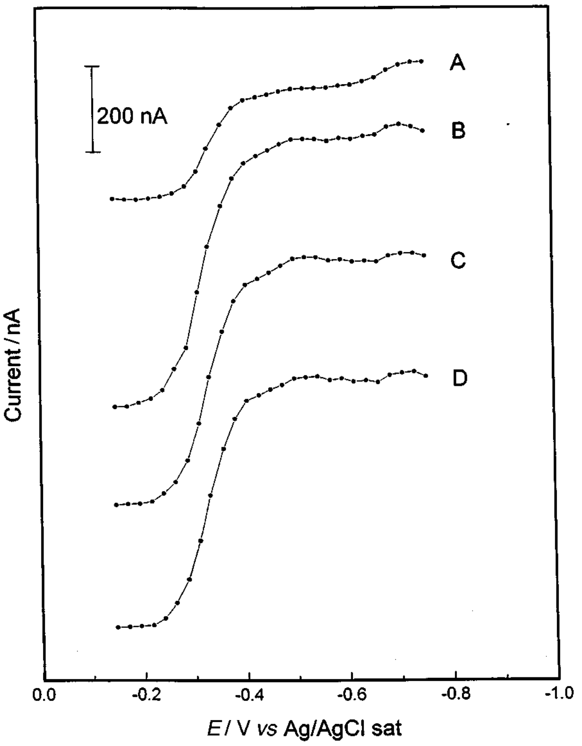

Fig. 5 A, pseudo voltammetric curve obtained using the cyclic matrix after a simulated multiplexed scan; B, pseudo voltammetric curve for a non-multiplexed multichannel electrode scan; C and D, pseudo voltammetric curve for the multiplexed scan using the cyclic matrix and 100 and 400 ms resting time intervals between multiplexed readings, respectively. A moving average weighted filter of five elements window was employed in all pseudo voltammetric curves. Data for solution containing 0.5 mmol l^{-1} Pb^{II} in 0.1 mol l^{-1} NaNO$_3$.

expected value of 2.78 predicted for the multiplexing theory when compared with the equivalent non-multiplexed electrode scan technique.

An overall evaluation of data obtained for this work reveals that any offset present at the current-to-voltage converter stage of the instrument is reduced as consequence of the use of the Hadamard technique. This reduction resulted from the fact that, after a Hadamard transform operation, any fixed value present in all multiplexed measurements is divided by $n/2$, where n is the number of independent electrodes present in the array.

Conclusion

The Hadamard multiplexed voltammetry proposed in this work shows that the S/N associated with independent electrodes in an array can be enhanced according the theory of multiplexing measurements. A full multiplex gain could not be achieved in the present case because the time interval spent to acquire the multiplexed signals was found to be higher than that predicted. This fact is a consequence of the voltammetric pulse techniques employed. Amperometric measurements, for example, should not suffer from the limitations caused by concentration depletion and a full multiplex gain could be attained. The reduction of the size of the electrodes in the array is another factor that will certainly decrease the resting time employed to recover the concentration of the electroactive specimen near the electrodes. Consequently, the multiplex gain should approximate more the ideal value.

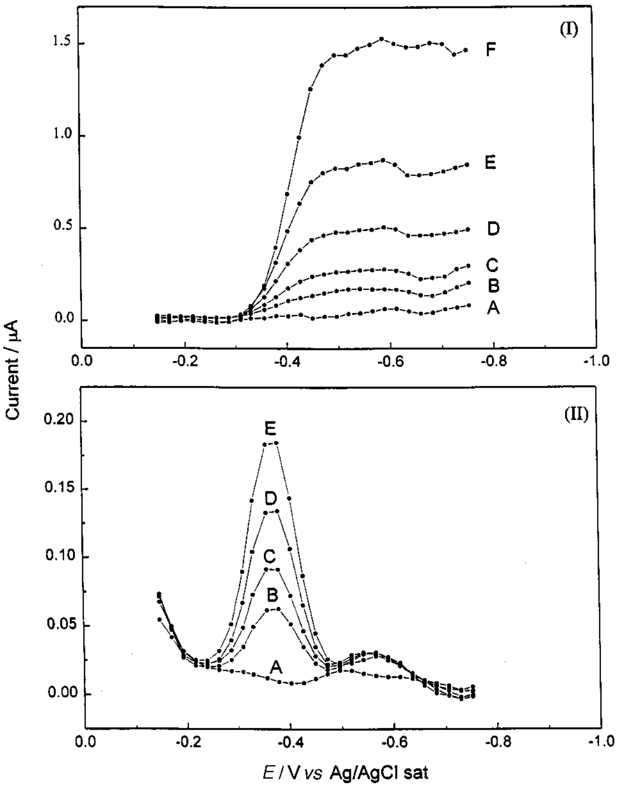

Fig. 6 Pseudo voltammetric curves obtained by the multiplexed technique showing the behaviour of the faradaic current as a function of the concentration of lead in 0.1 mol l^{-1} NaNO$_3$ solution. (I), normal pulse multiplexed technique (A, blank; B–F, 0.10, 0.19, 0.36, 0.66, and 1.17 mmol l^{-1} of Pb(II), respectively). (II), Differential pulse multiplexed technique (A, blank; B–E, 0.08, 0.11, 0.16, and 0.23 mmol l^{-1} of Pb^{II}, respectively). A moving average weighted filter of five elements window was employed in all voltammograms.

Table 1 Analytical curve statistical data obtained by the normal and differential pulse multiplexed techniques using the voltammograms shown in Fig. 6

Multiplexed technique	Slope ± s/ µA mmol^{-1} l	Linear coeff. ± s/µA	r	Error of estimate/ mmol l^{-1}
Normal pulse	1.083 ± 0.005	−0.006 ± 0.005	0.9999	0.008
Differential pulse	0.813 ± 0.002	−0.013 ± 0.01	0.9991	0.003

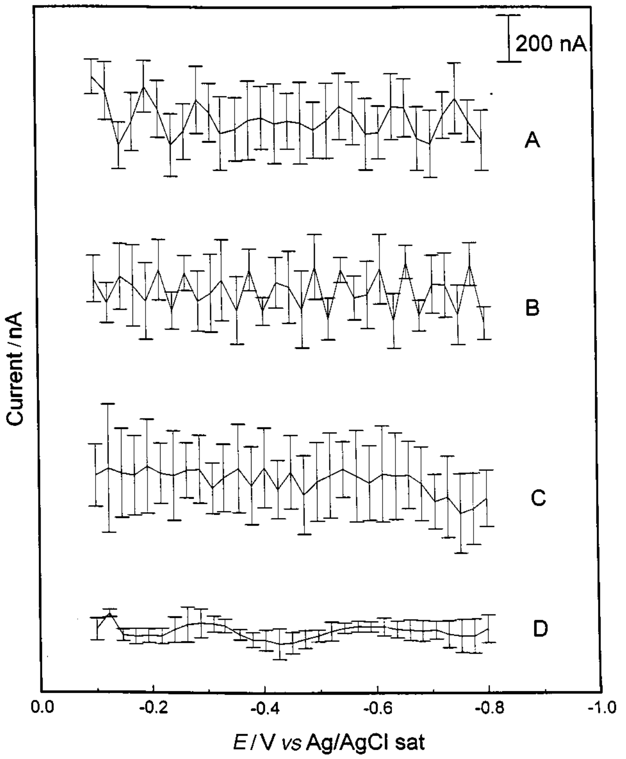

Fig. 7 Standard deviation of the residual current obtained by non-multiplexed and multiplexed differential pulse techniques of a blank electrolyte solution (0.1 mol l^{-1} NaNO$_3$) in the absence of cell electromagnetic shielding, for the 31 electrodes of the array. A, multi-channel non-multiplexed differential pulse electrode scan; B, differential pulse potential scan (one electrode); C, differential pulse potential scan (16 electrodes); and D, multiplexed differential pulse scan.

The proposed multiplexed approach has been evaluated for an array in which the individual characteristic of each electrode was only the applied potential. However, the multiplexed approach will be able to enhance the S/N for arrays in which each electrode is prepared to produce a selective response for a given analyte. In such cases, the combination of a group of microelectrodes to achieve a better S/N will be difficult and the multiplexed approach can be even more advantageous. Furthermore, the multiplexed technique could be employed for S/N improvement in other electrochemical techniques that use arrays of ion selective electrodes in potentiometry[24] and in conductimetric measurements such as in the 'electronic nose' sensors.[25]

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