

## Multi-electrode detection in voltammetry

### Part I. A versatile multi-channel voltammetric instrument

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**A multi-channel voltammetric instrument is described for use with arrays of micro-electrodes. The instrument can access up to 31 electrodes in voltammetric measurements either independently or in groups (2–31 electrodes per group) and works in a simple two electrode like cell model, employing only one current-to-voltage converter. Two digital-to-analog converters were employed to ensure wide flexibility of the potential applied to the array. The control of the instrument, the data acquisition and treatment procedures were automated using an addressable asynchronous interface and a microcomputer running software written in QuickBasic 4.5. An array, containing 31 microelectrodes, embodied in a polyester isolating block, was constructed and employed for evaluation of the instrument performance. Each microelectrode was made of a sub-array containing seven copper discs (55  $\mu\text{m}$  diameter) covered with a mercury film. Two new procedures to obtain voltammetric signals, at a scan rate equivalent to 3.2 V s<sup>-1</sup>, are proposed. These procedures access each electrode of the array while they are kept at different potentials, producing voltammetric pseudo-curves similar to those obtained by normal- and differential-pulse voltammetry. Other conventional voltammetric techniques such as potential staircase sweep, differential-pulse and anodic stripping voltammetry were also evaluated for use with the instrument, showing that the dynamic range of the measurements can be improved by selecting the number of electrodes to be employed without decreasing the scan rate.**

**Keywords:** Multi-channel voltammetric instrument; ultramicro-electrode arrays, voltammetric multi-channel detection

Interest in the use of arrays of micro-electrodes in voltammetry has increased in recent years. The first attempts to employ such arrays were aimed at increasing the signal-to-noise ratio (SNR) in liquid chromatography and flow injection detection by combining up to 100 electrodes while keeping the advantages associated with the size reduction of the electrodes.<sup>1,2</sup> In this approach, the arrays were used with conventional three electrode potentiostatic instruments.

A second stage in the use of arrays of electrodes began when specially constructed and/or adapted instruments allowed for independent access to the electrodes belonging to the array. In this approach, the most important feature is the ability to obtain the current associated with each electrode present in the array. Each electrode can, therefore, be considered as a sensor producing a distinct response (current) that is, in some way, a selective signal for an analyte present in the sample. This selectivity could, in principle, be achieved by modifying the electrode surface and/or by operating each electrode at a suitable potential. However, examples of the second type predominate.<sup>3–8</sup>

Instruments have been developed to operate with arrays of up to 16 electrodes of conventional millimeter size.<sup>3–5</sup> These

instruments employ the three electrode cell model and different potentials are generated to the working electrodes. However, to obtain the individual currents associated with each electrode, 16 current-to-voltage converters are necessary. To impart greater versatility to the system, up to 16 digital-to-analog converters have been employed in such instruments with the aim of applying distinct potentials to each working electrode.<sup>4</sup>

When the electrodes in an array have their size reduced from millimeter to micrometer dimensions, the electrochemical behavior shows improved characteristics.<sup>9</sup> The advantages of the use of electrodes of reduced size has been extensively described elsewhere<sup>9–15</sup> and will not be reviewed in detail here. However, it is important to point out the lower capacitive current, smaller ohmic drop and faster achievement of mass transport in a stationary diffusion state, followed by a higher current density, compared with electrodes of conventional size.<sup>9</sup>

There have been few reports dealing with multi-channel voltammetric instruments designed to employ arrays of electrodes of micrometer size.<sup>6–8</sup> Dees and Tobias<sup>6</sup> adapted a conventional potentiostat by adding 120 current-to-voltage converters that could be sequentially connected for readout through a 128 channel multiplexer. The instrument was used to access individually up to 100 square electrodes (98  $\times$  98  $\mu\text{m}$ ) arranged in a planar 10  $\times$  10 electrode matrix constructed with the objective of studying the interfacial mass transfer phenomena in electrochemical processes. Aoki and co-workers<sup>7,8</sup> described a multi-channel instrument dedicated to analytical determinations in a flowing medium. Sixteen band-like gold electrodes (0.1 mm wide, 3 mm long) were arranged sequentially and placed in a flow cell. In addition to the independent access to the 16 electrodes, a five step potential procedure allows for simulation of the resolution achieved by an 80 channel instrument. The instrument was employed for amperometric measurements. Therefore, the capacitive current is only important when the five step procedure is employed because the potential applied to the array needs to be changed.

All of the instruments described above<sup>3–8</sup> make use of the three electrode electrochemical cell model and do not exploit the possibility of using two electrode systems. The use of multiple current-to-voltage converters, found in the previously reported three electrode instruments, increases the complexity and the cost of constructing a multi-channel instrument. In contrast, it is recognized that ultramicro-electrodes (UMEs) can be used in electrochemical cells with only two electrodes owing to the small ohmic drop and negligible polarization of the reference electrode caused by such devices.<sup>16</sup> Even when hundreds of such UMEs are used in a group as a single working electrode, a low ohmic drop is observed.<sup>2</sup> Therefore, the use of arrays of UMEs appears to obviate the need for three electrode potentiostatic systems. Furthermore, it has been observed that, although the capacitive current can increase with the number of micro-electrodes present in an array, the rate of its decay is maintained after a potential pulse has been applied to the cell. In other words, the time constant of the cell is maintained regardless of the number of electrodes effectively employed in a voltammetric measurement.<sup>2</sup> This suggests the evaluation of

pulse techniques applied to multi-channel instruments be used as a replacement for the amperometric measurements usually employed.<sup>7</sup>

Arrays of UMEs can be produced using different materials. When individual measurements could be obtained from each electrode or group of electrodes, the arrays have been constructed with carbon fibers and noble metals such as Pt and Au.<sup>9</sup> Various geometric dispositions of the electrodes in an array have been adopted.<sup>17–22</sup> Disc-like surfaces arranged in a rectangular format are frequently found because they are relatively easy to construct.<sup>23</sup>

Micro-electrodes made of a mercury film (MFE) deposited over a substrate have been described.<sup>24–26</sup> Common substrates are carbon fibers, gold and platinum.<sup>9,19</sup> Copper can also be used as a substrate for MFEs. In addition to the low cost of this material, an electrode made with copper shows very good characteristics. The mechanical stability of the film is better than that of vitreous carbon and it compares well with platinum and silver.<sup>27</sup> A better hydrogen overpotential has also been reported for MFEs prepared on copper compared with gold, platinum and silver.<sup>27</sup> Among metallic cations usually employed in voltammetric studies, intermetallic specimens are reported to occur, to an appreciable extent, only for Zn during anodic stripping voltammetric experiments.<sup>24</sup> There are no reports on arrays of micro-electrodes that employ copper as a substrate for mercury film. Such electrodes could be employed to extend the use of arrays in order to work with stripping techniques with the consequent improvements in sensitivity that those techniques can offer.

This paper describes a multi-channel electrochemical instrument constructed to operate with arrays of UMEs. The instrument uses all the favorable characteristics of the micro-electrodes with dimensions in the micrometer range allowing for a simpler and cheaper electronic design while adding versatility to access the electrodes individually or in groups and to control the potential applied to the array. The use of the instrument along with an array constructed with 31 copper disc electrodes, covered with a mercury film, demonstrates its versatility and shows, for the first time, the possibility of employing this kind of UMEs in arrays.

## Experimental

### The multi-channel voltammetric instrument

Fig. 1 depicts the instrument constructed. The voltammetric system is based on a two electrode cell model. The counter-electrode (Ag/AgCl, in saturated KCl) is connected to a single current-to-voltage converter whose output is presented to a 12 bit analog-to-digital converter (ADC 7672). The area of the counter-electrode is about 10 times greater than the sum of the area of all the working electrodes. The 31 working electrodes (WE<sub>1</sub>–WE<sub>31</sub>) are connected to the potential control system through analog switches (ADG 201A) individually controlled by the microcomputer. The system for potential control consists of a voltage divider constructed with 30 metal film resistors (R<sub>1</sub>–R<sub>30</sub>) of 1 kΩ (±1%, 1/8 W) and two 8-bit digital-to-analog converters (DAC) (ZN 428). The potential differences applied to the working electrodes, coming from successive points of the divider, are buffered by quad-operational amplifiers (LM 348). Both the DACs can generate analog potentials in the range –1.8 to +1.8 V in steps of 14 mV. When both DACs operate at equal potential, their analog outputs are presented to all 31 electrodes. When they operate at different potentials, a staircase-like increasing potential value is generated over the electrode array. In the latter case, the potential applied to any working electrode ( $V_{wn}$ ) can be found from the equation

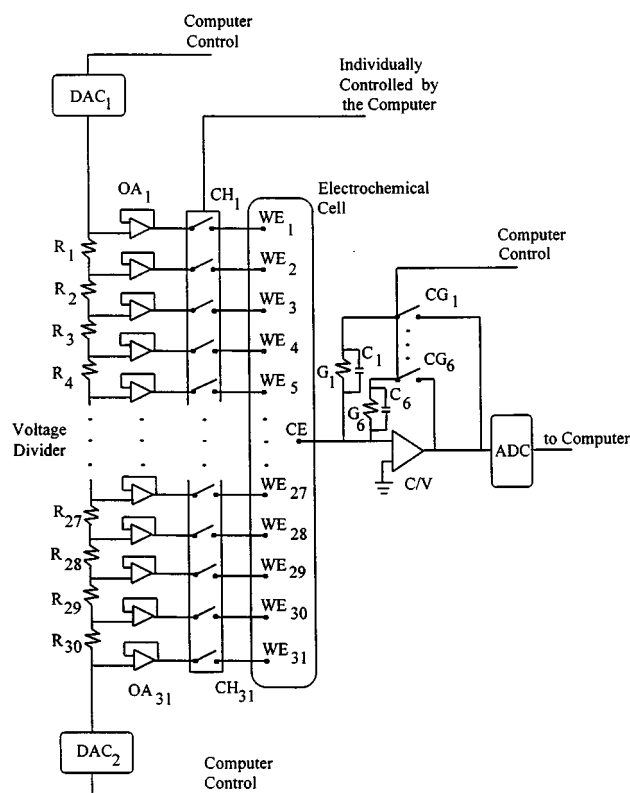
$$V_{wn} = V_{DAC1} + [(V_{DAC2} - V_{DAC1})/30](n - 1) \quad (1)$$

where  $V_{DAC1}$  and  $V_{DAC2}$  are the output voltage of DAC1 and DAC2, respectively, and  $n$  is the number of the electrode in the array ( $1 \leq n \leq 31$ ) (see Fig. 1), assuming  $V_{DAC1} < V_{DAC2}$ , which is normally the case.

The current-to-voltage converter can operate at six computer controlled gain values (current ranging from ±100 μA to ±100 nA) and was implemented based on an LF 356 operational amplifier. The gain selection was made also by using analog switches (AD 201A). The time constant for the current-to-voltage converter circuit was kept equal to  $150 \pm 5 \mu\text{s}$  for any of the six possible gain values.

### Computer hardware

A Zenith microcomputer compatible with an IBM-PC-286, 20 MHz, with a mathematical co-processor (80387) running at 20 MHz, 512 kbyte of RAM and 20 Mbyte, hard disc, was employed to control the multi-channel instrument and for data acquisition, treatment and storage. A user port constructed using an 8255 peripheral input/output device and an 8-bit parallel asynchronous interface (working in a handshaking mode for byte interchange) similar to that described previously<sup>28</sup> was employed. The interface has its own internal set of addresses used to access the devices necessary to control the multi-channel instrument and to perform data acquisition. Latches of 8-bits (74HC373) were employed to hold control bytes whose bit patterns are used to connect any electrode to the cell (through the analog switches) and to select the gain for the current-to-voltage converter. The present hardware, when driven by software written in QuickBasic 4.5, can acquire 12-bit resolution data (reading and storing in an indexed variable) in 254 μs.



**Fig. 1** Diagram of the multi-channel voltammetric instrument. OA, voltage buffers; CH, computer controlled analog switches for electrode connection to the cell; DAC, digital-to-analog converter; WE, working microelectrodes; CE, counter electrode; C/V, current-to-voltage converter; G, gain control circuit; CG, computer controlled analog switches for gain control; and ADC, analog-to-digital converter.

Therefore, the maximum sampling rate is 3937 data points per second.

### Electrode array

Fig. 2 shows the electrode array constructed and employed to evaluate the multi-channel instrument and to be used in various multi-channel or conventional voltammetric techniques. Initially, an array made of 31 individual copper wires, arranged in a circular format, was tried. The large differences among the responses of the electrodes indicated that it was necessary to employ more than one copper wire per electrode. The arrangement was then assembled employing sub-arrays of seven copper wires per electrode, each with a diameter of 55  $\mu\text{m}$ . A rectangular format was assigned to the array, as shown in Fig. 2. At one end, the seven wires of each sub-array were joined and soldered to a male Alphicon type 36-way connector to allow the electrodes to be accessed independently by the multi-channel instrument.

The distances among adjacent discs electrodes were set so as to avoid overlapping of their diffusion layers, namely greater than six times the wire diameter, as recommended previously.<sup>1</sup>

Electrical isolation and mechanical stability of the array were achieved by encasing the array in a polyester resin added in liquid form and cured for 24 h in a rectangular mold. The array was polished using abrasives of decreasing particle size. The last two were alumina of 1.0 and 0.3  $\mu\text{m}$ .

The exposed surfaces of the copper wires (discs) were washed with de-ionized water, immersed in 60% v/v phosphoric acid solution for 1 min and washed again with de-ionized water. Immediately afterwards, the array was immersed for 10 min in a 0.01 mol l<sup>-1</sup> solution of Hg(NO<sub>3</sub>)<sub>2</sub> containing 0.1 mol l<sup>-1</sup> HNO<sub>3</sub>, which allows for spontaneous mercury film deposition on the 217 copper discs of the array. The array was stored in 0.001 mol l<sup>-1</sup> (oxygen free) HNO<sub>3</sub> solution. Before use, the array was submitted to 60 voltammetric cycles applying a potential in the range 0.2 to -1.2 V at a 100 mV s<sup>-1</sup> scan rate in 0.1 mol l<sup>-1</sup> HNO<sub>3</sub> solution to homogenize the mercury film on the copper substrate.<sup>24</sup>

### Voltammetric Techniques

Voltammetric data were obtained by applying the excitation voltage to the electrode array in several modes. However, basically only two procedures need to be considered. In the first, during a scan, equal potential values are applied at the same time to one electrode, to a group of electrodes or to all 31 electrodes of the array. In this case, the electrode or the group operates as only one working electrode. These procedures will be termed potential scan (PS). In a PS procedure both DACs of the instrument will operate at the same output voltage, and no multi-channel feature is present. The signals generated ( $i \times V$  curves) are, therefore, true voltammograms obtained by conventional potential scan.

In the second kind of procedure, distinct potential values are applied to each electrode in the array, hence each electrode

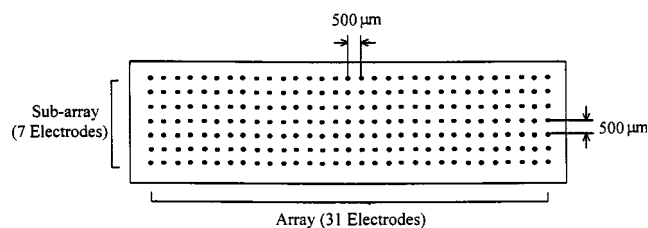


Fig. 2 View of the spatial distribution of the copper substrate micro-electrodes encased in a polyester resin. Seven copper wires (55  $\mu\text{m}$  diameter) are joined to form each electrode of the 31 present in the array.

operates as an individual sensor. The techniques employed to obtain the voltammetric signals in this way are termed electrode scan (ES) techniques. These techniques employ the multi-channel capabilities of the instrument. The 31 current values obtained for the 31 electrodes can be combined to produce a current  $\times$  potential pseudo-curve that should not be confused with true scan voltammograms.

Potential scan techniques include staircase sweep, triangular sweep (cyclic voltammetry), differential-pulse and differential-pulse anodic stripping voltammetry employed in the conventional way. The major difference is that the scan techniques employed in this work will always divide the range of potential to be scanned into 31 equal steps. This procedure was adopted in order to compare the results obtained by the PS techniques with those obtained by ES (multi-channel operation).

Electrode scan procedures can also be performed by using the excitation potential applied to each electrode in a way that is similar to that found in conventional differential-pulse voltammetry. In this case, a large amplitude pulse is applied to an electrode, the current is read and a small pulse with fixed amplitude (usually 50 mV) is subsequently applied over the initial potential. A new current measurement is made. The difference between the second and first measurements is taken as the analytical response.

All voltammetric measurements were obtained in a 50 ml capacity cell containing a initial volume of 25 ml of the supporting electrolyte solution (acetate buffer or sodium nitrate). A large Ag/AgCl counter electrode was always employed. The cell was placed inside a shielding cage to reduce environmental interference.

### Software and data treatment

The program to control the multi-channel instrument and to perform data acquisition and treatment was written in QuickBasic 4.5. The program is divided into two main modules, one employed for raw data acquisition and the other for data processing and display. The program is menu driven and all necessary instrumental parameters can be easily set by the user. In order to avoid undesirable timing alterations on the data acquisition sub-programs, due to DOS interruptions, the executable code was always employed.

Fig. 3 depicts two block diagrams illustrating the tasks performed by the software during the execution of a staircase sweep PS (A) and for the ES technique (B). In all voltammetric techniques employed the analog switches were activated, connecting the selected electrodes to the cell, before the excitation potential was applied. A resting potential (usually set at -0.1 V) was always applied before the excitation potential. Both procedures help to improve the reproducibility of the current measurements, avoiding the effect of the switching transients while the measurements are obtained from a well defined initial condition.

The user can request data treatment aiming at improving the precision of the current measurements. The averaging of a number of scans is the simplest method of data post-processing. The average current values are calculated and expressed along with their standard deviations.

It is also possible to apply a moving average filter to raw data employing variable window widths from two to five points. For two or three points the software calculates a non-weighted moving average. For the five point width the average is weighted attributing a weight of 3 to the central point of the window, 2 to the two immediate nearby points and 1 to the boundary points. These smoothing procedures are used only to reduce further the differences among the electrode responses in the ES technique (after the electrode correction described below has been applied). In this way, the final signals look more like

those obtained by classical PS techniques, allowing them to be easily compared.

### Correction for differences in the electrodes' responses

Data obtained by using the electrode scan (multi-channel) procedure can be corrected for differences in the responses of the electrodes. The correction procedure employs the faradaic current obtained for each electrode when excited by a fixed potential (greater than the half-wave potential) in a solution of an electroactive specimen. The median of the current values is employed in order to minimize the effect of electrode responses that present very different values on the corrected pseudo-curve

voltammogram.<sup>29</sup> Thirty-one correction factors are then calculated with the equation

$$f_n = \frac{i_n}{i_{\text{median}}}$$

where  $f_n$  is the correction factor for the  $n^{\text{th}}$  electrode,  $i_n$  is the current obtained for this electrode and  $i_{\text{median}}$  is the median of the 31 current values. The  $i_n$  values were obtained using similar conditions to those in the voltammetric technique for which the correction will be used. Fig. 4 shows a plot of typical values for the correction factors obtained for the electrodes of the array. Correction factors in the range 0.3–2 were found for the array during the experiments reported here. This response electrode

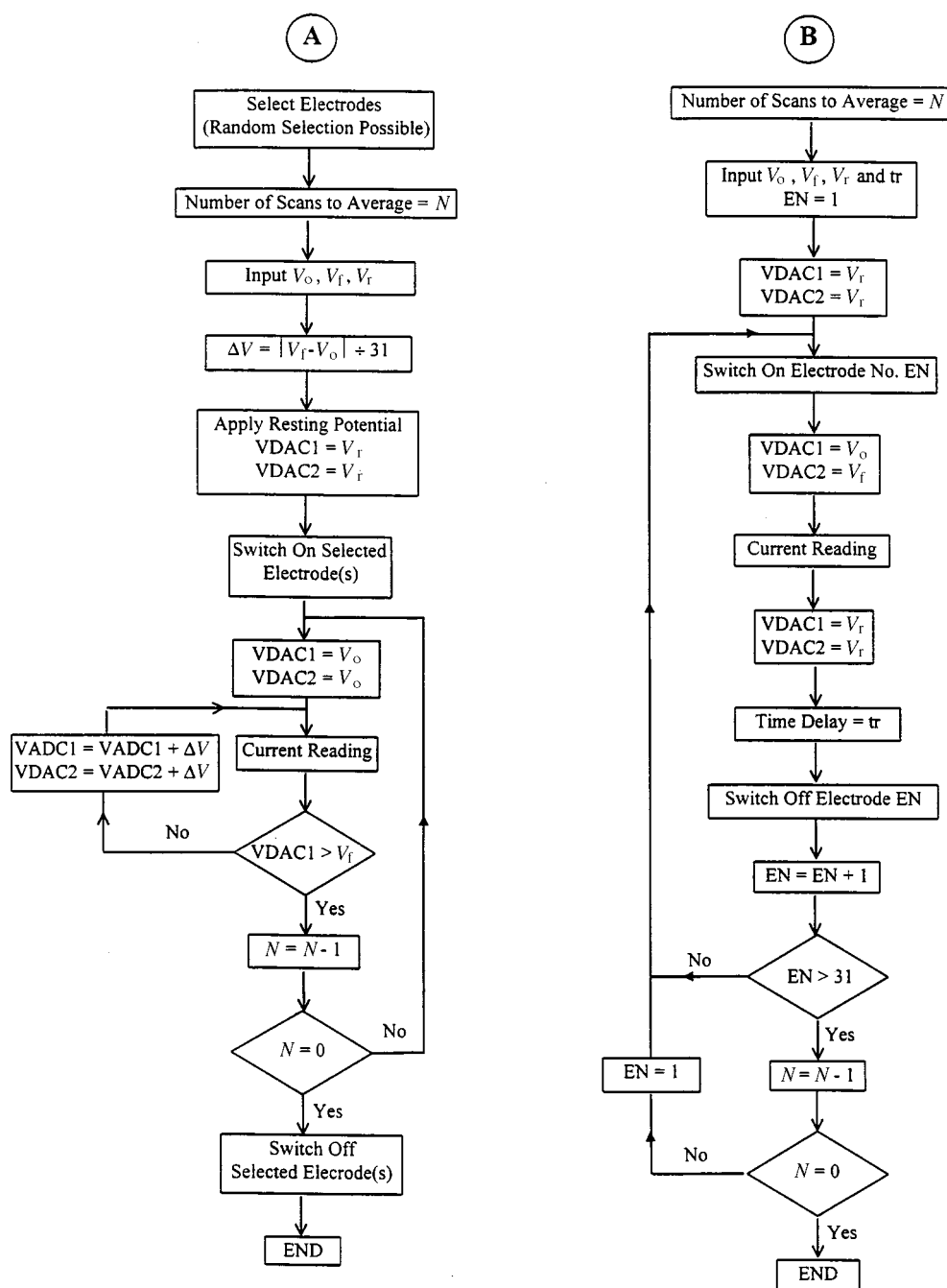


Fig. 3 Flow diagrams of the two main routines employed for voltammetric data acquisition from the electrode array by the proposed instrument. A, Sequence of operations for a staircase potential scan over a user defined number of electrodes; B, sequence for an electrode scan procedure.  $V_o$ , initial potential;  $V_f$ , final potential;  $V_r$ , resting potential; VDAC1 and VDAC2, output potential for digital-to-analog converter.

correction is necessary only to approximate the pseudo-voltammetric curves composed by the 31 electrode responses of an ES technique to the true scan voltammogram obtained by an equivalent PS technique.

### Reagents and solutions

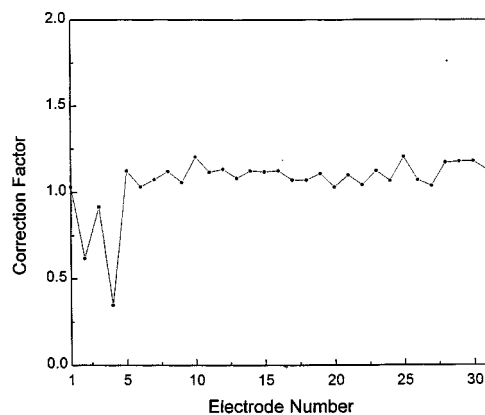
Analytical-reagent grade chemicals and freshly distilled, de-ionized water were employed throughout. Lead solutions were prepared from a  $4.831 \text{ mmol l}^{-1}$  stock standard solution made by dissolving 1.0000 g of the pure metal (Merck, Darmstadt, Germany) in  $1.0 \text{ mmol l}^{-1} \text{ HNO}_3$ . A stock standard cadmium solution of  $8.896 \text{ mmol l}^{-1}$  in  $1.0 \text{ mmol l}^{-1} \text{ HNO}_3$  was prepared from the pure metal (Merck). Acetate buffer solution (pH 4.7) was prepared from  $0.1 \text{ mol l}^{-1}$  acetic acid (Mallinckrodt, St. Louis, MO, USA) and  $0.1 \text{ mol l}^{-1}$  sodium acetate solution (Mallinckrodt). The supporting electrolyte solution was  $0.1 \text{ mol l}^{-1}$  sodium nitrate (Merck). Films of mercury were prepared employing a solution  $0.01 \text{ mol l}^{-1}$  of  $\text{Hg}^{\text{II}}$  in  $0.1 \text{ mol l}^{-1} \text{ HNO}_3$  obtained from polarographic grade (99.9999%) metallic mercury (Carlo Erba, Milan, Italy).

### Results and discussion

The main characteristic of the instrument developed is its high versatility. The present configuration allows single- and multi-channel electrochemical techniques to be performed using the same array of electrodes. In the multi-channel ES approach, each electrode of the array can be viewed as a set of 31 different sensors. The response of those sensors (current) produced in the presence of different analytes and its dependence on their concentrations is, in the present case, a result of the potential applied to a specific electrode.

Owing to its design, the instrument always works, in any multi-channel technique, by applying pulses of increasing potential amplitudes to the electrodes. An ES procedure, for instance, is produced by applying increasing potential pulses, one pulse for each electrode, and reading the resulting current.

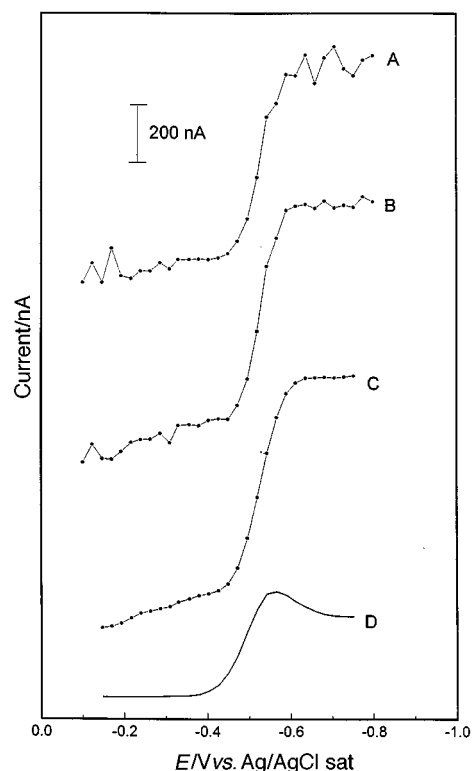
Fig. 5(A) shows a typical pseudo-voltammetric curve achieved by ES of the array obtained for a  $\text{Cd}^{\text{II}}$  solution. Fig. 5 also shows (B) the pseudo-voltammetric curves after the correction factors have been employed to minimize the differences among the responses of the 31 electrodes and (C) the resulting curve after use of the five point moving average filter. Each current value shown in Fig. 5 was obtained in a time interval of 227 ms and, therefore, at an equivalent scan rate (for



**Fig. 4** Correction factors obtained for an electrode scan of the array. The values show that electrodes 2 and 4 present a large current response to the same electroactive specimen concentration. Data obtained for a solution containing  $0.6 \text{ mmol l}^{-1} \text{ Cd}^{\text{II}}$  in  $0.1 \text{ mol l}^{-1} \text{ NaNO}_3$  solution; all electrodes at  $-0.80$  versus  $\text{Ag}/\text{AgCl}$ .

the 31 electrodes) of  $3.2 \text{ V s}^{-1}$ . The equivalent scan rate with the ES multi-channel technique does not have the same meaning as in conventional potential ramp techniques. The scan rate, in this case, refers to the ratio between the range of amplitude of the pulsed potential and the time necessary to collect the 31 current data. In this way, the equivalent scan rate reflects more the electrode scan rate than the potential scan rate. Successive scans made by the ES technique show that reproducible results are obtained for the current values associated with each electrode. Therefore, it is demonstrated that the 200 ms time interval spent in a scan is sufficient to regenerate the original concentration of the analyte around the electrode surface.

Fig. 5(D) shows a true voltammogram obtained for a single electrode (composed of seven copper wires) when a conventional staircase like potential scan is employed. Thirty-one potential steps were applied to the same electrode and the currents were acquired in the same time interval as in the ES technique. The voltammogram shows the typical behavior of a static solid-state electrode<sup>10</sup> with the current reaching a peak and decreasing towards a steady-state value. An interesting result obtained with the ES technique is that the pseudo-voltammetric curve resembles the one that should be obtained, for example, if a dropping mercury electrode is employed in a PS procedure. A steady value of the faradaic current is obtained (observed differences are accounted for by geometric differences among electrodes). The value of the average faradaic current obtained by the ES technique is almost twice that of the peak value of the current obtained by the PS technique. To confirm a good comparison, the electrode selected for PS showed a response for the faradaic current very close to the median value for the 31 electrode responses. Additional experiments showed that in the PS technique the faradaic current goes straight to a steady-state value (without peaking)

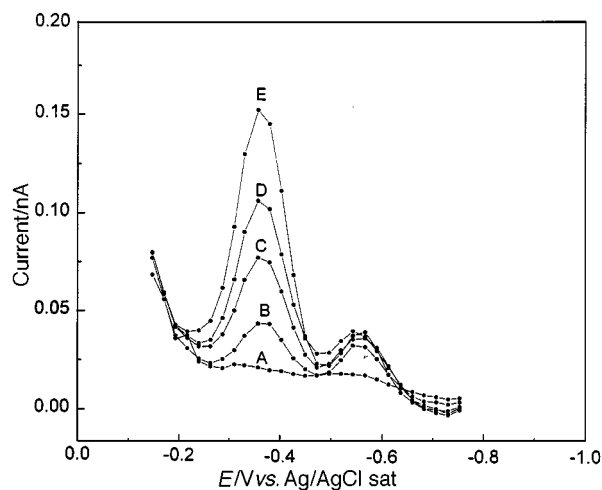


**Fig. 5** Pseudo-voltammetric curves obtained by the electrode scan multi-channel technique for a solution containing  $0.6 \text{ mmol l}^{-1} \text{ Cd}^{\text{II}}$  in  $0.1 \text{ mol l}^{-1} \text{ NaNO}_3$ . Reference electrode,  $\text{Ag}/\text{AgCl}$ . A, Original data; B, data after applying the correction factors found in Fig. 3; C, data after weighted moving average; and D, a true voltammogram obtained for the potential scan technique at the same equivalent scan rate of  $3.2 \text{ V s}^{-1}$ .

only when the scan rate is decreased to  $160 \text{ mV s}^{-1}$ . Under these conditions the maximum faradaic current is reduced even more (by about 80%) in relation to that observed in the ES technique.

Differential-pulse techniques have been employed to reduce the effect of capacitive current over the analytically useful faradaic current. The ES procedure can adopt a similar approach by taking the faradaic current after application of a pulse to an electrode, storing it and taking another current value for a small amplitude pulse applied over the main pulse. The difference between the currents can be related to the potential of the main pulse and a peak like signal is obtained for the pseudo-voltammetric curve. Fig. 6 shows the resulting curves for various solutions of  $\text{Pb}^{\text{II}}$  obtained by this multi-channel technique, termed here differential-pulse electrode scanning (DPES).

When the instrument was not employed in the multi-channel mode, it was possible to observe that the faradaic current generated by each electrode is additive. Table 1 shows calibration results for the faradaic current obtained for  $\text{Pb}^{\text{II}}$  solutions with concentrations in the range  $0\text{--}1.88 \text{ mmol l}^{-1}$  and when one or 16 electrodes were employed in the potential scan. The ratio between the two slopes is 16.6, showing the additive behavior of the faradaic current. Obviously, the ratio is not exactly equal to 16 as the electrodes do not present the same current response for a given applied potential. Additive behavior of the currents was also observed when the number of electrodes was increased in a PS procedure for a solution containing  $\text{Cd}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ . Fig. 7 shows some voltammograms obtained by increasing the number of electrodes employed in the scan from 1 to 31. Table 2 shows the relationship between the faradaic current and the number of electrodes. The linear behavior also attests that the currents are additive.



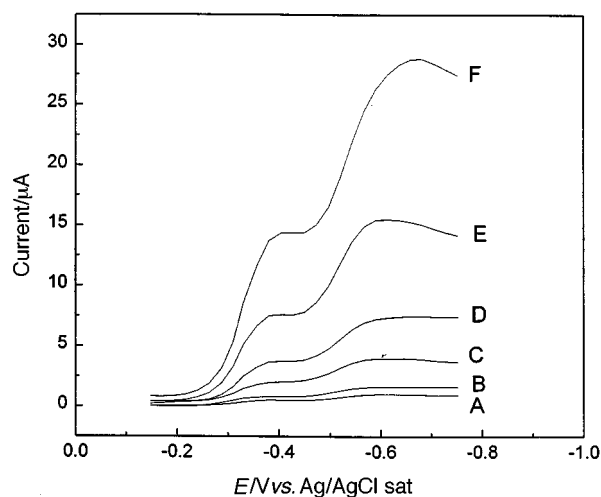
**Fig. 6** Pseudo-voltammetric curves obtained by the differential pulse electrode scan technique (DPES) for  $\text{Pb}^{\text{II}}$  in  $0.1 \text{ mol l}^{-1} \text{ NaNO}_3$ . A, Blank; B, C, D and E, signals for  $\text{Pb}^{\text{II}}$  solutions at  $0.044$ ,  $0.081$ ,  $0.111$  and  $0.161 \text{ mmol l}^{-1}$ , respectively

**Table 1** Data for the analytical curves obtained for  $\text{Pb}^{\text{II}}$  in  $0.1 \text{ mol l}^{-1} \text{ NaNO}_3$  solution by the conventional staircase PS technique with one and a group of 16 electrodes.  $R$ , regression coefficient;  $s_a$ , standard deviation of the slope;  $s_b$ , standard deviation of the linear coefficient;  $S$ , error of the estimate.  $\text{Pb}^{\text{II}}$  concentration in the range  $0.1\text{--}1.88 \text{ mmol l}^{-1}$

PS (No. of electrodes)	Slope/ $\mu\text{A l mmol}^{-1}$	Linear coefficient	$R$	$s_a$	$s_b$	$S$
1	0.594	-0.019	0.9998	0.005	0.005	0.008
16	9.87	-0.25	0.9998	0.08	0.08	0.1

For PS techniques, the possibility presented by the proposed instrument of employing a user defined number of electrodes can be viewed as an additional way to expand the dynamic range of the voltammetric measurement. Lower concentrations can be accessed by using all the available electrodes of the array and higher concentrations could be determined with only one electrode. With electrodes of the size reported here, and in agreement with previously reported results,<sup>2</sup> the cell time constant appears to suffer very small changes when the number of electrodes included in the measurement is increased. Therefore, the scan rate is not decreased as the sensitivity is increased by using more electrodes in a measurement. Additive behavior of the faradaic current was also observed for other potential based scan techniques such as differential-pulse and anodic stripping voltammetry.

Detection limits (DL) for  $\text{Pb}^{\text{II}}$  were obtained for all the techniques employed by using three times the signal-to-noise ratio determined for small signals obtained near the lower extreme of the concentration range for each technique, to allow a more realistic calculation of these values. Table 3 gives the DL values obtained for each technique. It is not surprising that the DLs obtained for anodic stripping voltammetry are lower owing to the preconcentration characteristic of this technique. A comparison between ES and PS techniques shows that large amplitude multi-channel techniques (ES) can reach lower detection limits. However, the effect of using one electrode for each potential is annulled when small amplitude techniques, such as DPES, are employed in the multi-channel approach. This occurs because the gain in the faradaic current (obtained in the ES technique mainly by depletion of the analyte present around the electrode before pulse application) is not found after the second pulse necessary for the DPES technique. In fact, in this case, a worse detection limit is observed for the multi-channel approach whereas a significant improvement in the DL



**Fig. 7** Voltammograms obtained by the conventional potential scan technique. Fixed  $\text{Pb}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  concentrations of  $0.7$  and  $0.6 \text{ mmol l}^{-1}$ , respectively. A, B, C, D, E and F, voltammograms obtained by one electrode and by joining 2, 4, 8, 16 and 31 electrodes, respectively, of the array.

**Table 2** Analytical curve data obtained by the PS technique for the data in Fig. 7. Parameters as in Table 1

Specimen	Slope/ $\mu\text{A}$ per electrode	Linear coefficient	$R$	$s_a$	$s_b$	$S$
$\text{Pb}^{\text{II}}$	0.464	-0.03	0.9997	0.005	0.08	0.1
$\text{Cd}^{\text{II}}$	0.468	-0.03	0.9998	0.005	0.07	0.1

is observed for its single-channel counterpart (the staircase potential scan technique).

Parallel to the observation of instrument performance, the behavior of the array of copper microelectrodes covered with mercury film was evaluated. The array shows very good stability for Pb<sup>II</sup> and Cd<sup>II</sup> determinations by using the different techniques described here, including stripping procedures. For an evaluation made during 7 d using the ES technique and a Pb<sup>II</sup> solution (0.500 mmol l<sup>-1</sup> in 0.1 mol l<sup>-1</sup> NaNO<sub>3</sub>) and performing a total of more than 2000 scans, without film replacement, the array shows a mean relative standard deviation for the limiting current of 2.7%. In order to achieve this stability, the whole electrode array must be submitted daily to 60 cyclic voltammetric scans in 0.1 mol l<sup>-1</sup> HNO<sub>3</sub> from 0.2 to -1.3 V at a scan rate of 100 mV s<sup>-1</sup>. This procedure was employed for mercury film regeneration over the copper substrate, as proposed by Donten and Kublik<sup>24</sup> in their study of a single copper electrode of conventional size. The good performance of the electrode array ensured confidence in the evaluation of the performance of the proposed instrument.

The main drawback observed when working with such UMEs was the differences in response obtained for some electrodes in some of the arrays tested. Usually, as shown in Fig. 4, an electrode (electrode 4, for instance) or some electrodes give faradaic currents that exceed by more than twofold the mean value calculated for the other electrodes in the array. However, this distinct current value is still proportional to the concentration of the electroactive specimen. This fact and the reproducibility obtained for the current generated for such electrodes allows the conclusion that some leakage, due poor resin adhesion, may have caused an increase in the exposed active surface area of these electrodes.

## Conclusion

A versatile voltammetric instrument has been developed to be employed with arrays of microelectrodes. The use of UMEs allow for a simple design of the multi-channel instrument and the use of multi-channel scan techniques where each electrode is viewed as an independent sensor. Owing to its simplicity, the number of independent electrodes could be easily increased above the 31 employed in this work, without any serious change in the electronic design. In fact, the same current-to-voltage converter can be used and only an inexpensive electronic buffer, a resistor and an analog switch need be added for each new electrode. Obviously, better techniques to produce the electrode arrays, such as metal deposition and microlithography, could be employed in that case.

The resolution obtained in multi-channel techniques (minimum potential difference applied between two successive electrodes) could be increased by including more electrodes in an array. However, the use of two digital-to-analog converters

in the proposed instrument allows the user to restrict the range of potential in which an electrode scan will be obtained. In this way, a closer look at the behavior of the voltammetric signals, with higher resolution in a restricted range of potential, can be achieved.

The number of sensors employed in each measurement is defined by the user and can be employed to expand the dynamic range of concentration capable of being determined. The faradaic current was observed to be additive for all techniques employed in the present work whereas, owing their small size, the cell time constant appears to be independent of the number of electrodes employed in a measurement. This feature can be added to the electronic gain control, normally found in voltammetric instruments, in order to increase their dynamic range.

The characteristics shown by the proposed instrument allow the prediction of many interesting applications in analytical procedures and electrochemical studies employing voltammetric detection techniques.

The independent access to each electrode conferred by the instrument suggests its use along with true arrays of sensors where each surface of each electrode (and not only the potential applied to it) can be prepared to make its response selective to a given analyte. In this case, the potential applied to each sensor (electrode) perhaps does not need be presented as increasing values (ramp-like), as set by the potential divider net of resistors employed in this work. Instead, different resistor nets could be used to apply the necessary potential to each electrode. The possibility of working, in the multi-channel approach, with up to 31 distinctly modified electrodes would exploit the maximum potential of the proposed instrument.

The use of the instrument in kinetic studies will facilitate data acquisition in time intervals as short as 65 μs. Concerning this application, the potential where the electroactive specimen of interest is to be monitored could be applied to both DAC converters and the electrode scan technique employed to acquire the current for the 31 electrodes, each one looking at the concentration of the specimen after a time interval of 65 μs. It is important to recall that the reduction in the size of the electrodes can permit one to increase even more the equivalent scan rate for the ES technique, resulting in a better time resolution in kinetic experiments.

The instrument can be used to follow the effect of time or potential on the deposition of electroactive specimens, helping in the development of stripping and adsorptive techniques because the data could be accessed simultaneously in a single experiment.

Owing to the random access allowed by the instrument, it could be used to obtain combined measurements with groups of any number of electrodes and in any order, maintaining their individual characteristics, given, in the present case, by the applied potential. Such a capability should be evaluated to employ the instrument in multiplexed data acquisition procedures which, owing their nature, would improve the detection limits while keeping the data acquisition speed and electrode identity unchanged.

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**Table 3** Detection limits for Pb<sup>II</sup> observed for the different techniques by using the proposed instrument and the electrode array of mercury film over copper substrate

Type	Technique	Detection limit for Pb <sup>II</sup> /μmol l <sup>-1</sup>
Multi-channel techniques	ES	9
	DPES	32
Conventional techniques	PS (1 electrode)	42
	PS (16 electrodes)	6
	PS (16 electrodes)	6
	DPPS (1 electrode)	18
	DPPS (16 electrodes)	3
	DPPS (31 electrodes)	1
	DPASV (1 electrode)	0.089
	DPASV (16 electrodes)	0.018

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