

Comparison of direct current, derivative direct current, pulse and square wave voltammetry at single disc, assembly and composite carbon electrodes: stripping voltammetry at thin film mercury microelectrodes with field-based instrumentation

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A comparative investigation of normal and stripping forms of voltammetry was undertaken at single and random array microdisc, macrodisc and composite carbon electrodes using dc, derivative dc, square-wave and differential-pulse waveforms. Studies on the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ in 0.05 M KNO_3 revealed that the dc waveform with derivative readout is superior to the use of square-wave or differential-pulse waveforms at both single disc and random array carbon fibre electrodes. Analytical superiority to that obtained at a conventional glassy carbon macrodisc electrode was also observed. The detection limit for the determination of $[\text{Fe}(\text{CN})_6]^{3-}$ was 4×10^{-6} M at the carbon fibre random array microdisc electrode and 6×10^{-6} M when using a single disc microelectrode (scan rate = 200 mV s^{-1}). For the determination of Pb and Cd in 0.1 M HCl by stripping voltammetry, the ideal combination of high sensitivity (≥ 1 ppb detection limit), avoidance of the need to remove oxygen or utilise solution stirring or electrode rotation could be achieved at mercury-plated thin film single disc or random array microelectrodes or composite electrodes. Furthermore, under these thin film conditions, the analytical performance of each of these three electrode types improved with respect to signal-to-background current ratio as the scan rate increased. Consequently, short potential scanning times as well as optimum sensitivity are achieved with scan rates in the $1\text{--}50 \text{ V s}^{-1}$ range. All of the results obtained demonstrate that highly sensitive field-based voltammetric analysis may be accomplished using the combination of an inherently simple two-electrode battery operated instrument, the dc waveform and random array or single carbon fibre microdisc working electrodes. An interface which enables voltammetric studies to be undertaken with a battery operated personal computer is described for this purpose.

Keywords: Voltammetry; microdisc and related electrodes; direct current and transient waveforms; battery operated instrumentation

than conventional macrodisc electrodes include the possibility of not requiring the need for removal of oxygen, nor rotation of the electrode or stirring of the solution in stripping voltammetry. Consequently attractive features for their use in field based studies are now emerging.

Several classes of microelectrode are available for trace analysis. These include the single microdisc electrode, arrays of microdisc electrodes, line electrodes and composite particle electrodes. The last two classes of electrode are usually fabricated in large numbers at very low cost using lithographic or equivalent technology and may be regarded as single use disposable electrodes, whereas the first two classes of electrode may be regarded as re-useable rather than disposable. While each of these different classes of electrodes may be manufactured from different materials, the well recognised electro-analytical advantages of carbon has made this the preferred material in the majority of analytical applications.

When macrodisc electrodes are used, square-wave, differential-pulse or other transient forms of voltammetry are commonly used in voltammetric analysis because of the more favourable faradaic-to-charging current ratio than that obtained with the simple dc waveform.⁴ However, when microelectrodes or electrodes that exhibit microelectrode type behaviour are operated under steady-state, or near steady-state conditions, the charging current is extremely small, so whether any advantages can be gained by using the more complex transient waveforms is debatable.

In this study, a comparison of macro- and microelectrode performance was initially undertaken with both transient and dc waveforms using commercially available laboratory forms of instrumentation. These comparative studies utilised glassy carbon macrodisc, single disc and array carbon fibre and composite carbon particle electrodes with both diffusion controlled and thin film stripping forms of voltammetry. After confirming the advantages of the use of electrodes exhibiting microelectrode type behaviour and establishing that the dc or its derivative is the optimum waveform for their use, a battery operated personal computer form of instrumentation was developed for use in field-based applications of stripping voltammetry.

Experimental

Initial experiments using mains powered laboratory-based equipment were undertaken with a Cypress Systems Model CS 1087A electrochemical system for cyclic, dc (staircase), derivative dc, square-wave and differential pulse voltammetry and a Bioanalytical Systems BAS-100A Electrochemical Analyzer for stripping voltammetry.

A block diagram of the electrochemical interface developed during the course of this investigation and which can be used

The wide availability of low powered electronic circuitry and battery operated microcomputers has meant that portable battery operated field-based voltammetric instrumentation can now be readily developed.¹ However, the question as to which electrode types are optimum for use with field based instrumentation has yet to be considered in detail. In the last two decades microelectrodes have become widely available and they have found numerous applications in trace analysis.^{2,3} Some of the advantages of the use of microdisc electrodes rather

with a battery operated personal computer based instrument is given in Fig. 1. The electrochemical interface is built around an Analog Devices AD7868 12 bit serial analogue-to-digital/digital-to-analogue converter. The output voltage from the D/A section is supplied to an electrode *via* a low output impedance unity gain buffer. The measured current is converted to voltage by a current-to-voltage converter which has three software-selectable current ranges. Data and control lines of the AD7868 are connected to a PC's parallel port. A bipolar waveform of any shape, fully controlled by the software, can be produced by the instrument, although only data obtained *via* a staircase ramp are reported in this paper. The interface was designed with ease of usage, portability and low power requirements in mind and can be used with any IBM-PC compatible computer equipped with a standard Centronics parallel port. The interface is particularly suitable for use in the field with portable computers, but can be used with equal ease with a desktop computer.

The specifications listed below apply to the interface:

- (a) Resolution: 12 bits for output voltage and input current. Resolution can be increased to 14 bits by use of AD7869, which is a 14 bit A/D D/A converter, pin compatible with AD7868.
- (b) Output voltage: $\pm 3\text{V}$ bipolar.
- (c) The maximum scan rate depends on the speed of the computer and is 6000 mV s^{-1} using the 66 MHz 486 computer employed here.
- (d) Input current: three selectable ranges, determined by the value of resistors in the current-to-voltage converter. The most sensitive range used in this work was $\pm 30\text{ nA}$ bipolar.
- (e) Power supply: 9 V batteries.
- (f) Dimensions $12 \times 5 \times 3\text{ cm}$.

Additional details related to the hardware and software associated with the electrochemical interface may be obtained from the authors on request. A 5 ml capacity glass electrochemical cell containing the required working electrode, aqueous Ag/AgCl (saturated KCl) reference electrode and platinum wire auxiliary electrode (for studies with a three-electrode potentiostated system) was used in all voltammetric experiments. The working electrodes were a $5\text{ }\mu\text{m}$ radius carbon fibre microdisc electrode, a $3.5\text{ }\mu\text{m}$ radius carbon fibre random assembly microdisc array electrode (median nearest neighbour distance of approximately $70\text{ }\mu\text{m}$) manufactured by CSIRO Australia under the RAM trade mark,^{5,6} a 1 mm radius glassy carbon macrodisc electrode and graphite thin film disposable electrodes containing carbon micro particles embedded in epoxy which are produced by IVA (Ekaterinberg, Russia).⁷

Initial experiments were undertaken at $20\text{ }^{\circ}\text{C}$ using $\text{K}_3[\text{Fe}(\text{CN})_6]$ and the one-electron reduction process $[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$ in aqueous media with 0.05 M KNO_3 as the electrolyte. In this series of experiments, results obtained from dc (staircase) voltammetric experiments and their

derivatives were compared with square wave and differential-pulse voltammograms in the presence and absence of oxygen, *i.e.*, with and without the solution being de-gassed with high purity nitrogen.

A further series of experiments using laboratory based instrumentation were undertaken at $20\text{ }^{\circ}\text{C}$ with non-deoxygenated and non-stirred 0.1 M HCl solutions using the stripping voltammetric response for the two-electron oxidation of Pb and Cd as their amalgams to Pb^{II} and Cd^{II} , respectively, from *in situ* mercury coated carbon electrodes. Variation of the stripping responses as a function of mercury plating solution concentration, deposition potential, scan rate and deposition time was examined. Finally, stripping voltammetric experiments were undertaken with the home-built electrochemical interface and battery operated PC to confirm that equivalent performance to that obtained with commercially available laboratory-based instrumentation could be achieved with a simple form of battery operated instrument that can be used in a field environment. Standard solutions of Hg^{II} , Cd^{II} and Pb^{II} used in the stripping voltammetry were prepared by dilution of BDH atomic absorption spectrometric (AAS) standard solutions.

There is, of course, an inherent problem with respect to a valid comparison of data, which is related to the influence of the level of filtering applied to the different forms of voltammetric experiment, particularly when data are obtained from a range of instruments, as is the case in this study. Hence, the pragmatic approach was adopted of always applying the minimum level of filtering required to remove high frequency random noise. In this way, the background current was believed to represent closely that resulting from the electrochemical experiment, rather than from extraneous random noise.

Results and discussion

Studies with microelectrodes using mains powered laboratory-based instruments

Reduction of $[\text{Fe}(\text{CN})_6]^{3-}$

Initial studies focused on a comparison of voltammograms obtained at the single and random array carbon fibre microdisc electrodes and the conventional glassy carbon macrodisc electrode for the process



When using the dc (staircase) waveform, the expected sigmoidal shaped curve is observed when using the single disc or array microdisc electrodes (Fig. 2) at slow scan rates. However, the sigmoidal wave shape, which requires the use of the limiting current to determine the concentration, is not competitive, in the analytical sense, with the peak-shaped responses obtained with the square-wave or differential-pulse waveforms. Consequently, the derivative form of the dc technique, which gives a peak shape akin to that found when using transient square and pulse waveforms, was chosen for the purposes of evaluation of concentration detection limits.

Fig. 3 shows a comparison of data obtained using different waveforms and the three electrode types mentioned in the paragraph above for reduction of $1.0 \times 10^{-4}\text{ M } [\text{Fe}(\text{CN})_6]^{3-}$ in water with 0.05 M KNO_3 as the supporting electrolyte. Clearly, with the random array and single disc microelectrodes, the square-wave, differential-pulse and dc (staircase) derivative voltammograms are essentially equivalent in the analytical sense, using the experimental parameters contained in the legend to Fig. 3. That is, each combination of electrode and waveforms produces voltammograms with well defined peaks and an excellent signal-to-noise (background) ratio at the 10^{-4} M concentration level, under the specified conditions. Furthermore, it is clear that the voltammograms obtained at the

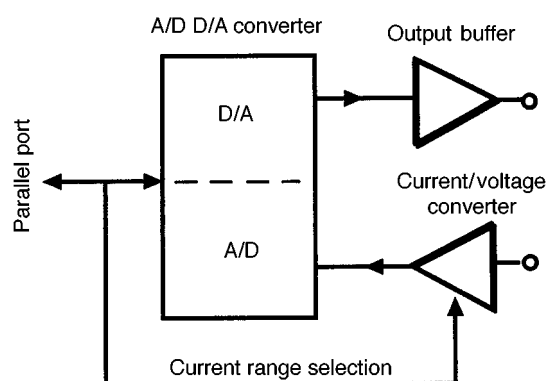


Fig. 1 Block diagram of a battery powered electrochemical interface that can be used with a personal computer.

microelectrodes have a superior signal-to-background current ratio to that obtained with a conventional glassy carbon electrode at a scan rate of 200 mV s^{-1} . Thus, in the analytical sense, superior response will be achieved with the microelectrode forms of electrode, when used under near steady-state rather than transient conditions.

Examination of voltammograms obtained at a $[\text{Fe}(\text{CN})_6]^{3-}$ concentration of 10^{-5} M , which is approaching the detection limit, reveals that the derivative dc (staircase) plots provide the flattest background and best signal-to-background current ratio, with the signal-to-noise ratio at the array electrode being superior to that obtained with the single microdisc electrode. Interestingly, at the 10^{-5} M concentration level and conditions given in the legend to Fig. 3, the square wave response is only marginally above the background current level except at the RAM electrode. For all electrode and technique combinations,

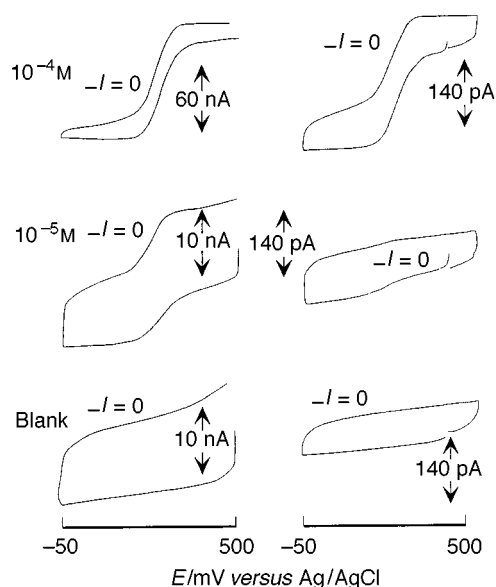


Fig. 2 Dc (staircase) voltammograms obtained as a function of concentration for reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ in aqueous 0.05 M KNO_3 electrolyte at random assembly (left hand side) and single disc (right hand side) carbon fibre microelectrodes. Scan rate = 200 mV s^{-1} .

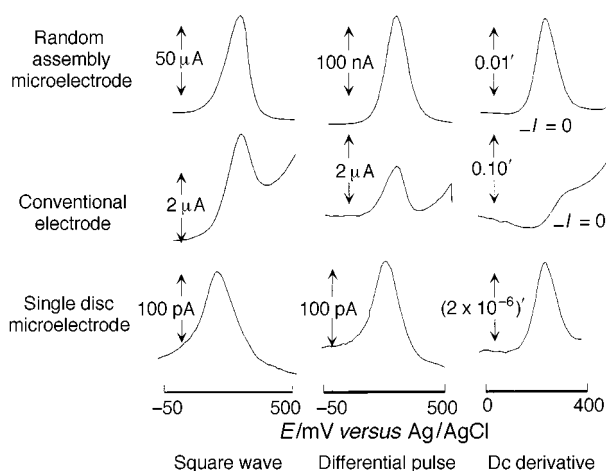


Fig. 3 Comparison of square-wave (step height = -6 mV , amplitude = -30 mV , square wave period = 30 ms), differential-pulse voltammograms (step width = -10 mV , pulse height = -50 mV , cycle period = 50 ms) and dc (staircase) derivative (scan rate = 200 mV s^{-1}), for reduction of $10^{-4} \text{ M } [\text{Fe}(\text{CN})_6]^{3-}$ in aqueous 0.05 M KNO_3 at random assembly and carbon fibre single microdisc and macrodisc glassy carbon electrodes.

voltammograms obtained at the $10^{-6} \text{ M } [\text{Fe}(\text{CN})_6]^{3-}$ concentration level are essentially indistinguishable from those obtained from the blank solution containing no added $[\text{Fe}(\text{CN})_6]^{3-}$.

Studies on voltammograms obtained over the concentration range from 10^{-4} to $10^{-6} \text{ M } [\text{Fe}(\text{CN})_6]^{3-}$ enabled detection limits to be determined using the experimental conditions given in the legend to Fig. 3. The concentration detection limit using the derivative dc readout form was calculated to be $4 \times 10^{-6} \text{ M}$ for the array electrode and $6 \times 10^{-6} \text{ M}$ for the single disc electrode. These detection limits were determined from the concentration when the signal-to-noise (background) ratio is 3:1. At the glassy carbon macroelectrode, the detection limit was found to be greater than 10^{-5} M with all waveforms, whilst differential pulse voltammetry at the RAM electrode produced a detection limit of $7 \times 10^{-6} \text{ M}$, which was the lowest value obtained with transient methods at a microelectrode. These data imply that the derivative dc technique at a microelectrode already provides optimum or close to optimum performance in the analytical sense and that the use of transient waveforms at microelectrodes, unlike the case prevailing at macroelectrodes, offers no significant intrinsic improvement in analytical sensitivity. This feature of microelectrode voltammetry arises because the ready access to the steady-state or near steady-state response virtually eliminates charging current. The use of transient methods with microelectrodes requires the measurement of smaller currents than with the dc technique and since there is no significant charging current to compensate under steady state conditions, the advantage of using transient waveforms no longer exists. In contrast, at the glassy carbon macrodisc electrode, the advantage of the transient waveform is clearly revealed. In this case, when the voltammograms are obtained under transient conditions, a relatively large charging current is present which is discriminated against *via* use of a square wave or differential-pulse method.

Experiments on the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ when the derivative dc technique was used at the microdisc electrodes over the concentration range from 5×10^{-6} to 10^{-4} M were independent of whether oxygen was present or absent, within the limit of experimental error. Data referred to in Fig. 3 and discussed above refer to experiments in which oxygen was removed by de-gassing with high-purity nitrogen. A slight variation in the dc background current was observed before a derivative was taken when oxygen was not removed, but this feature is not evident when using the derivative form of the readout. That is, the concentration detection limits given above on the basis of data obtained when nitrogen de-gassing was used were also achieved when oxygen was present. In contrast, slightly higher blank levels were evident and the detection limit slightly increased when using the differential-pulse or square-wave techniques in the presence of oxygen. Thus, the derivative dc technique at the microdisc array electrode still remains the preferred technique when oxygen is present.

Dc voltammograms at the random array microdisc electrode were also examined as a function of scan rate over the range $50\text{--}200 \text{ mV s}^{-1}$. For scan rates in excess of 200 mV s^{-1} , mass transport by linear rather than radial diffusion becomes significant as does the background or charging current as significant departures from the steady-state regime emerge. Indeed, at scan rates of 200 mV s^{-1} or greater, the array electrode starts to acquire the characteristics of a macrodisc electrode and the analytical performance deteriorates accordingly. An equivalently less favourable situation is also obtained at a single disc microelectrode, when using fast scan rates. Thus, a scan rate of $\leq 200 \text{ mV s}^{-1}$ was found to be optimum for analytical voltammetry when using single or array microdisc carbon fibre electrodes having radii of around $3\text{--}5 \text{ }\mu\text{m}$. At low scan rates, departures from the sigmoidal shape are minor so that the derivative response is symmetrical, and a minimal contribution arises from the charging current.

Anodic stripping voltammetry at mercury thin film microdisc electrodes

After establishing that no advantages exist when using microelectrodes with transient rather than dc waveforms, the important analytical problem of determining heavy metals by anodic stripping voltammetry was examined extensively at array and single microdisc carbon fibre electrodes with the dc staircase waveform. With the stripping technique and the dc waveform, a peak-shaped response is obtained without the need to take the derivative. After the optimum operating conditions had been found with these electrodes, comparison of data was made with those found when using disposable composite graphite-epoxy electrodes which, as noted elsewhere, also exhibit microelectrode like behaviour.⁷ All stripping data reported below with 0.1 M HCl as the electrolyte are independent of whether or not solutions were de-gassed with nitrogen to remove oxygen.

In situ stripping voltammetric experiments with 10^{-5} – 10^{-3} M Hg^{II} and 20 ppb Pb and Cd concentrations, revealed that the presence of 10^{-4} M Hg^{II} as the mercury plating solution gave extremely well defined stripping voltammograms with excellent reproducibility when using a scan rate of 400 mV s^{-1} and a deposition potential of -900 mV (see Fig. 4). Under these conditions, the peak height for the Pb and Cd stripping processes increased linearly with deposition time over the range 1–30 min at both the random array and single microdisc carbon fibre electrodes. An almost linear dependence of peak height on scan rate was also observed with scan rates over the range 0.1 – 50 V s^{-1} at both classes of microdisc electrode. Since the background current exhibited a smaller dependence on scan rate than the stripping peak, the signal-to-background current ratio

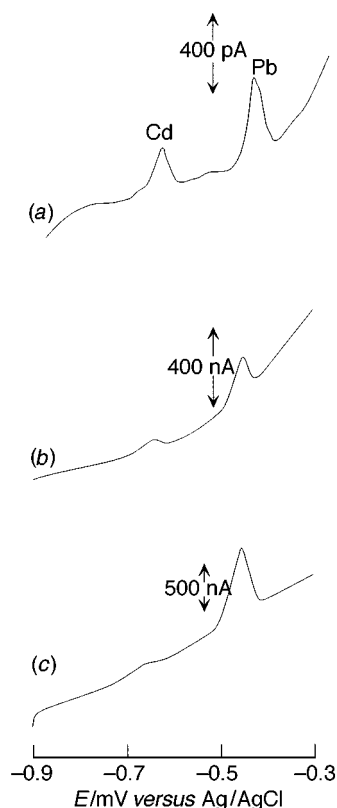


Fig. 4 Anodic stripping voltammograms obtained from 20 ppb solutions of cadmium(II) and lead(II) in 0.1 M HCl at mercury plated thin film (a) single disc carbon fibre microelectrode, (b) random assembly carbon fibre microdisc electrode and (c) disposable composite graphite-epoxy electrode. Scan rate = 400 mV s^{-1} , deposition potential = $-900 \text{ mV versus Ag/AgCl}$, deposition time = 60 s, $[\text{Hg}^{\text{II}}] = 1 \times 10^{-4} \text{ M}$.

at *in situ* mercury plated microelectrodes initially improved as the scan rate increased, becoming optimum at scan rates of around 10 V s^{-1} (Fig. 5). This improved analytical performance at high scan rate has also been reported at composite graphite disposable electrodes⁶ and is a useful feature of stripping voltammetry at mercury film microelectrodes. The fact that a similar improvement in analytical performance also occurs with increasing scan rate at the mercury film glassy carbon macrodisc electrode suggests that this feature is a function of the use of mercury thin film electrodes, rather than arising from factors associated with the use of microdisc electrodes. The dependence of the detection limit for the determination of Pb, again calculated as the concentration at which the signal-to-background current ratio is 3 : 1, on scan rate is presented in data contained in Fig. 5. The determination of 1 ppb Pb^{II} in 0.1 M HCl requires a scan rate of 10 V s^{-1} at the random array electrode, whereas a scan rate of 25 V s^{-1} is required to achieve this detection limit at the single disc microelectrode, with a deposition time of 1 min. Use of a 10 min deposition time and a scan rate of 10 V s^{-1} gives a detection limit of 0.1 ppb for the determination of Pb at the random array electrode.

The disposable graphite-epoxy composite electrodes also exhibit similar characteristics to those reported with microdisc electrodes, although significant differences in the ratios of the peak heights for the Cd and Pb stripping process are evident (Fig. 4).

Overview of results obtained with microelectrodes

In summary, microelectrodes, in either assembly or single disc forms, achieve excellent analytical responses when using staircase dc waveforms. With electrode radii in the $5 \mu\text{m}$ range and scan rates of the order of 200 mV s^{-1} , derivative dc voltammetric performance has been found to be superior to that obtained with square wave or differential pulse waveforms for a diffusion controlled process. Transient techniques also require the use of lower scan rates and longer experimental times. In the stripping mode at mercury thin film microelectrodes, dc (staircase) scan rates of around 10 V s^{-1} may be used to achieve

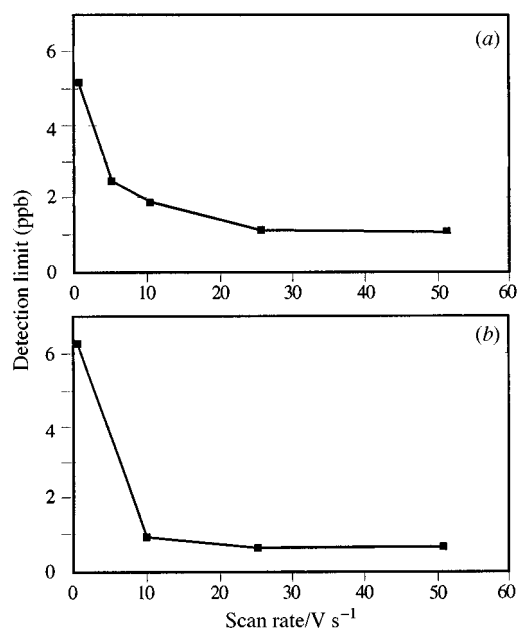


Fig. 5 Detection limits for the determination of lead in 0.1 M HCl by anodic stripping voltammetry as a function of scan rate at (a) single microdisc and (b) random assembly carbon fibre microdisc electrodes. Deposition potential = $-0.900 \text{ V versus Ag/AgCl}$, deposition time = 60 s, $[\text{Hg}^{\text{II}}] = 1 \times 10^{-4} \text{ M}$.

high sensitivity without the need for removal of oxygen or solution stirring or electrode rotation. Finally, a potentiostated three-electrode system is not required to achieve the above-mentioned performance when microelectrodes are used in aqueous media. In fact, experiments conducted in a two-electrode mode inherently have less noise present. Interestingly, whilst the use of an array microdisc electrode was found to be superior in performance to a single disc microelectrode with respect to limit detection, the improvement is relatively marginal. Small currents can be measured readily with modern forms of instrumentation, so that the detection limit is predominantly determined by the ratio of the electrochemical signal-to-background current ratio, rather than noise.

The above results imply that the construction of a battery operated portable instrument for field based voltammetric analysis with microelectrodes is moderately simple, because all that is required is the generation of a dc (staircase) waveform which can be applied at scan rates in the $1\text{--}10\text{ V s}^{-1}$ range, measurement of current as a function of dc potential, use of a non-potentiostated two-electrode system (single or array microdisc working electrode and a reference electrode) and a suitable data acquisition system. All these features are readily achieved with the aid of a standard battery operated 'lap top' computer, and a low powered interface of the kind described under Experimental.

Voltammetric studies with microelectrodes using the portable battery operated field based instrument

The home-built instrument described under Experimental employs a two-electrode, rather than a three-electrode potentiostated cell system. Noise levels are suitably low because mains frequency 'pick up' is avoided with the battery operated device. In principle, all that is required is to attach the voltammetric interface to a 286, 386, 486 or Pentium PC or its equivalent and develop suitable software that enables the staircase waveform to be generated. The applied potential and measured current values are then stored in the data acquisition system and analysed *via* use of standard software packages. The current-voltage curve (or its derivative) can also be displayed on the screen on the microcomputer if visual inspection of the voltammogram is required.

Fig. 6 illustrates a stripping voltammogram obtained for the determination of Cd and Pb using the random array microdisc electrode and the field-based instrument with a scan rate of 3 V s^{-1} . Because of inherently low noise levels obtained with battery operated equipment, this 'unsmoothed' voltammogram is equal or better in quality with respect to signal-to-noise ratios than that obtained with mains powered potentiostated laboratory-based instrumentation. With the field-based instrumentation, the potential and current at any place on the curve can be read. If required and *via* the use of standard software, the operator can also zoom in on any part of the voltammogram to give, for example, only the Pb response, and moving point averaging or other forms of smoothing can be implemented. Thus, the combination of a 'lap top' PC system, a two-electrode electrochemical cell employing a microelectrode working electrode and a low powered interface represents an extremely powerful approach to field based trace analysis. Thus, in

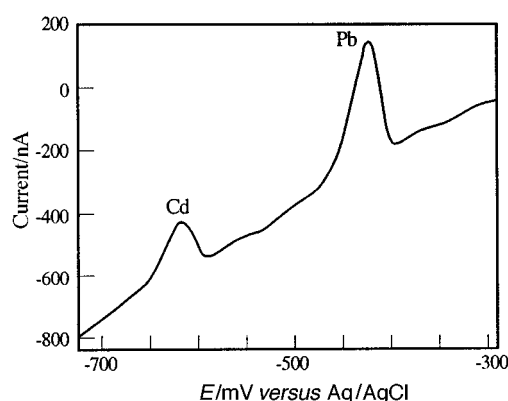


Fig. 6 Stripping voltammograms obtained with the field-based instrument for a 10 ppb solution of both cadmium(II) and lead(II) in 0.1 M HCl at a mercury plated thin film random assembly microdisc electrode. Scan rate = 3 V s^{-1} . Deposition potential = $-900\text{ mV versus Ag/AgCl}$, $[\text{Hg}^{2+}] = 1 \times 10^{-4}\text{ M}$, deposition time = 60 s. Data displayed over potential range from -750 to $-300\text{ mV versus Ag/AgCl}$.

situations where an analytical voltammetric method has been developed for use in the laboratory, there is a high probability that a dc staircase or derivative staircase method applied with a microelectrode will be ideal for use in the field based applications. Ideally, with this microelectrode-battery operated instrument combination, solution de-gassing to remove oxygen and stirring of solutions or electrode rotation can also be avoided in applications utilising stripping voltammetry. These last features minimise power requirements as well as the complexity of the experiments, which is essential for field-based voltammetric studies.

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References

- 1 Bond, A. M., Hudson, H. A., Tan, S. N., and Walter, F. L., *Trends Anal. Chem.*, 1988, **7**, 159, and references cited therein.
- 2 *Ultramicroelectrodes*, ed. Fleischmann, M., Pons, S., Rolison, D. R., and Schmidt, P. P., Datatech Systems, Morgenton, NC, 1987, and references cited therein.
- 3 Bond, A. M., *Analyst*, 1994, **119**, R1, and references cited therein.
- 4 Bond, A. M., *Modern Polarographic Methods in Analytical Chemistry*, Marcel Dekker, New York, 1980, and references cited therein.
- 5 Deutscher, R. L., and Fletcher, S., *J. Electroanal. Chem.*, 1988, **239**, 17.
- 6 Fletcher, S., *Chem. Austr.*, 1994, **61**, 80.
- 7 Brainina, Kh. Z., and Bond, A. M., *Anal. Chem.*, 1995, **67**, 2586.

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