Square-wave Anodic Stripping Voltammetry in Stationary and Flowing Solution: a Comparative Study*

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A comparison has been made between square-wave anodic stripping voltammetry (SWASV) at a stationary, mercury thin-film electrode and at a wall-jet mercury thin-film electrode in flowing solution using cadmium(II) and lead(II) as test species. Mercury thin films were prepared on glassy carbon electrode substrates. The effects of square wave amplitude and frequency on the peak current and peak potential in the determination step were studied, and these parameters optimized. Deposition time was varied, and the effect of flow rate in flowing solution investigated. Practical detection limits were found to be $10^{-8} \text{mol} \cdot \text{L}^{-1}$ at stationary electrodes and $2 \times 10^{-9} \text{mol} \cdot \text{L}^{-1}$ at wall-jet electrodes. It was found that SWASV gives good results in the presence and absence of dissolved oxygen for both analysis modes, which augurs well for its future application in flow systems, and particularly at wall-jet electrodes.

**Keywords:** Square-wave anodic stripping voltammetry; mercury thin-film electrode; wall-jet electrode; lead; cadmium

**Introduction**

Stripping voltammetry as a technique for the determination of trace levels of many chemical species is now well established.\(^1\) Recent advances have centred on improving the analysis time and decreasing the detection limit by using novel pulse techniques,\(^2\) particularly square-wave voltammetry (SWV).\(^3\) Square-wave voltammetry is a large-amplitude pulse technique, which measures difference currents, and is faster and more sensitive than other pulse techniques. Anodic stripping voltammetry (ASV) for determining trace metals in solution using the square-wave pulse form in the determination step (SWASV) offers several advantages with respect to differential-pulse anodic stripping voltammetry: a more rapid determination step, hence decreasing total analysis time and increasing sample throughput, no necessity to remove dissolved oxygen from solution, and higher sensitivity.

In analytical determinations, high sample throughput and good reproducibility and repeatability can be aided by performing determinations in flow systems, either in continuous flow\(^4\) or by flow injection (FI).\(^6\) Both of these approaches are applicable to on-line monitoring, with the possibility of switching flow streams in or out, and ensure that fresh solution is monitored in consecutive determinations. This is not necessarily the case for batch analyses in quiescent or stirred solution.

The coupling of square-wave techniques with flow systems is therefore of particular interest in order to take advantage of the benefits of both these approaches.

In this work, comparison was made between SWASV at a stationary mercury thin-film electrode in stirred solution and at a wall-jet mercury thin-film electrode in flowing solution. Square-wave anodic stripping voltammetry at stationary electrodes has been the subject of previous studies, e.g., see refs. 7–9. A number of applications of the wall-jet electrode to the stripping voltammetry of trace metals in solution have been described. These used linear-sweep, differential-pulse or the ring-disc collection technique in the determination step, e.g., refs. 10–12, but none has yet involved square-wave voltammetry. The particular advantage of the wall-jet electrode is that the impingement of a fine jet solution on the centre of a disc electrode, which then spreads out radially, ensures that the electrode always receives fresh solution and suffers no concentration-depletion effects.

Parameters affecting the voltammetric response, such as square-wave frequency and amplitude and deposition time were investigated, as well as the presence of oxygen in solution, using cadmium(II) and lead(II) as test species. The relative merits of SWASV at stationary electrodes in stirred solution and in flowing solution at wall-jet electrodes are assessed.

**Experimental**

For stationary-electrode experiments, a glassy carbon (GC) electrode of 3.0 mm diameter was used, linked to an Amel Model 433 polargraphic analyser, which includes a stirrer in the electrode stand. The auxiliary electrode was a platinum wire and the reference an Ag–AgCl (saturated KCl) electrode. Experiments were controlled through a PC 286 with Amel software, which permits the programming of the entire ASV experiment. The stirrer was activated during the preconcentration step (600 rev min\(^{-1}\)), and was stopped during the determination step.

Wall-jet electrode experiments were conducted with an Oxford Electrodes wall-jet cell containing a GC disc electrode of 3.0 mm diameter, a platinum tube counter electrode in the cell exit, and an Ag–AgCl (3 mol L\(^{-1}\) KCl) reference electrode; the nozzle diameter was 0.0345 cm. The solution was pumped from a reservoir by a Gilson Minipuls 3 peristaltic pump through a 3 m length of PTFE tubing (0.8 mm i.d.) to the wall-jet cell. Flow rates were measured gravimetrically. Electrical connection was made from the wall-jet cell to the Amel Model 433 polarographic analyser, and experiments were controlled as for those using the stationary electrode.

After polishing the glassy carbon electrodes with alumina (1 μm particle size) and setting-up the cell, mercury and

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cadmium and/or lead were co-deposited on the glassy carbon electrodes at −1.0 V for periods up to \( t_{\text{dep}} = 600 \) s, where \( t_{\text{dep}} \) is the deposition time. Square-wave stripping from −1.0 to −0.4 V, at frequencies varying from 20 to 500 Hz and with varying square-wave amplitudes, was employed in the determination step. Electrochemical cleaning at +0.4 V versus the reference for 30 s was sufficient to ensure good reproducibility between determinations.

All solutions were prepared from analytical-reagent grade chemicals and Millipore Milli-Q water (resistivity 18 MΩ cm). Stock solutions of 10−3 mol l−1 Cd2+ and Pb2+ were prepared from the nitrate salts in plastic calibrated flasks; 10−2 mol l−1 Hg2+ was prepared from the chloride salt. The supporting electrolyte in all studies was 0.10 mol l−1 NaClO4, to which aliquots of the other solutions were added (after appropriate dilution) by means of Eppendorf digital pipettes. Unless stated otherwise, solutions were not de-oxygenated.

**Results and Discussion**

Results obtained using stationary and wall-jet electrodes show a number of important differences and will be presented separately, followed by a comparison of their relative sensitivities and detection limits.

**Stationary Electrodes**

Typical SWASV traces for cadmium and lead are shown in Fig. 1; the stripping peaks are almost symmetrical. The peak potentials, −0.622 and −0.548 V, respectively, agree well with those obtained using differential-pulse ASV, and have the advantages of a larger peak current (\( I_p \)) and more rapid scan (2 s instead of 150 s). Hence, medium exchange can be avoided and there is not sufficient time for significant alterations to the electrode surface. Comparison between oxygenated and de-oxygenated solutions showed no difference in the peak currents, the only effect being in the oxygenation step. Electrochemical cleaning at −0.4 V, at frequencies varying from 20 to 500 Hz, and with varying square-wave amplitude (\( h \)) on the peak current, \( I_p \), is shown in Fig. 2(a) and (b) for lead and cadmium. Within the selected ranges, there is a good linear relationship between peak current and deposition time was found for both lead and cadmium, Fig. 2(c). Calibration plots for the two metal ions, obtained under the following conditions \( f = 100 \) Hz, \( h = 30 \) mV, and \( t_{\text{dep}} = 180 \) s, yield slopes of 0.82 and 0.93 A mol−1 for cadmium and lead, respectively. In practice, the detection limits achievable are of the order of 10−8 mol l−1; although from signal precision (i.e., the noise level) a detection limit of \( \approx 10^{-10} \) mol l−1 is predicted.13

Analysis of solutions containing both Cd and Pb is possible as the differences in peak potentials in the stripping of the two

![Fig. 1 Typical SWASV results obtained at a stationary electrode in stirred solution for Cd and Pb. Experimental conditions: square-wave frequency, 100 Hz; amplitude, 30 mV; \( t_{\text{dep}} = 180 \) s; [Cd2+], 9.28 × 10−8 mol l−1; and [Pb2+], 9.12 × 10−8 mol l−1.](image1)

![Fig. 2 SWASV of \( \bullet \), Pb and \( \blacksquare \), Cd at a stationary electrode in stirred solution. (a) Effect of square-wave frequency, \( f \), on peak current at 30 mV amplitude; (b) effect of square-wave amplitude, \( h \), on peak current at \( f = 100 \) Hz; and (c) plots of peak current versus deposition time, \( t_{\text{dep}} \) (Pb, \( f = 100 \) Hz, \( h = 30 \) mV; and Cd, \( f = 200 \) Hz, \( h = 30 \) mV). Other conditions: (a) and (b), [Pb2+] = 4.77 × 10−8 mol l−1; [Cd2+] = 4.76 × 10−8 mol l−1, and \( t_{\text{dep}} = 180 \) s; and (c), [Pb2+] = 1.97 × 10−8 mol l−1, and [Cd2+] = 2.50 × 10−8 mol l−1.](image2)

![Fig. 3 Cadmium and lead mixtures: (a) typical SWASV stripping curve: [Pb2+] = 9.12 × 10−8 mol l−1, and [Cd2+] = 9.28 × 10−8 mol l−1; and (b) calibration graphs ([Cd2+] = [Pb2+]). Conditions: \( f = 100 \) Hz; \( h = 30 \) mV; and \( t_{\text{dep}} = 180 \) s.](image3)
metals from the mercury thin film are sufficient to permit good resolution. The potentials for the stripping peaks are \(-0.553\) and \(-0.630\) V, and are therefore very similar to those obtained from solutions containing only one of the cations. A typical stripping curve is illustrated in Fig. 3(a), and Fig. 3(b) shows the respective calibration graphs. The slopes of these graphs are \(0.68\) and \(0.97\) A mol\(^{-1}\) l for Cd and Pb, respectively. Hence there is a noticeable decrease in the sensitivity of the cadmium signal, accompanied by a slight increase of the lead peak, when compared with results from solutions containing only one of the ions. It is not very clear why this should occur. A possible explanation is that the presence of lead within the mercury makes the transport of cadmium from the bulk to the surface of the mercury more difficult; this could lead to a lower peak height in the difference current from square-wave voltammetry. If this explanation is correct, then at hydrodynamic electrodes, the effect should be less, owing to the increased concentration gradient in aqueous solution due to the thin diffusion layer. This will be discussed further later in this paper.

Wall-jet Electrodes in Flowing Solution

The same types of experiment detailed earlier were conducted at wall-jet electrodes. The higher mass transport means that it is not useful to test all the different experimental conditions described earlier. In particular, it was found that SWASV could not be performed on samples with metal ion concentrations higher than \(10^{-7}\) mol l\(^{-1}\). This will be discussed further later in this paper.

Typical wall-jet electrode SWASV results are shown in Fig. 4. The peak potentials are almost equal to those at stationary electrodes \((-0.628\) and \(-0.554\) V), particularly when the measured difference in the potential of the two reference electrodes, one of which contained saturated KCl (stationary-electrode cell) and the other 3 mol l\(^{-1}\) KCl (wall-jet cell), of 11 mV is taken into account. The peak shapes are now less symmetrical, which is to be expected at hydrodynamic electrodes, where the concentration gradient in solution is steeper than at stationary electrodes. However it should also be noted that, whereas the signal for lead was larger than that for cadmium at stationary electrodes, here the opposite is true. This will be discussed further later in this paper. It can also be seen that the background current is increased and that the baseline is less horizontal. Nevertheless, this does not compromise the calculation of peak currents.

The equation for the diffusion-limited current, \(I_L\), at the wall-jet disc electrode\(^{14}\) is

\[
I_L = 1.43nFC\nu D^{3/2}V^{-1/2}\gamma^2\rho_{2}\Sigma_{c_0}^{l/4}n_{dep}^{1/4} \frac{V}{V^2}
\]

where \(D\) is the diffusion coefficient of the electroactive species, \(V\) the volume flow rate of the solution of viscosity \(\nu\), \(a\) the nozzle (i.e., jet) diameter, \(r\) the electrode radius, and \(c_0\), the bulk concentration of electroactive species. Therefore it is predicted that the amount of metal deposited in the pre-concentration step should be proportional, not only to the deposition time, \(t_{dep}\), but also to \(I_L\), and, consequently, to \(V^2\), because the deposition potential is chosen corresponding to the diffusion-limited current. The particular wall-jet cell employed had a very fine nozzle, so that high sensitivities could be expected to be achieved, as has been shown in differential-pulse ASV,\(^{15}\) and ASV with collection at a concentric wall-jet ring electrode.\(^{10}\) The linearity of peak current with \(V^2\) over a wide range of flow rates is shown in Fig. 5 for lead. Deviations at very low and very high flow rates are to be expected. At very low flow rates, the contribution from radial diffusion, which is neglected in the theoretical treatment described earlier as being small in comparison with radial convection, cannot be ignored; this leads to enhanced contact between the incoming fresh solution and the electrode. At high flow rates, there are two possible factors: first, the confined space in the wall-jet cell causes the hydrodynamic velocity profile to be affected, and secondly, there is a tendency for a lower adhesion of the mercury film to the glassy carbon substrate, especially near the centre of the disc electrode. Both these factors lead to lower than expected currents at high flow rates. From the flow rate variation of peak current, it was decided to use a flow rate of 0.0045 cm\(^3\) s\(^{-1}\) in subsequent experiments. This is sufficiently high to ensure negligible radial diffusion effects in the wall-jet hydrodynamics within the wall-jet cell, whilst not consuming excessive amounts of solution.

The effect of square-wave frequency on the results at the wall-jet electrode was evaluated. It was found that at low frequencies (\(<50\) Hz), the peak current was small, then rose linearly, and began to tail off at 200 Hz. A possible explanation of the high square-wave frequency behaviour involves coupling of the electrode kinetics with mass transport, which does not occur at stationary electrodes. It was also found that larger amplitudes for the square-wave form were necessary, the optimum being 50 mV, in contrast to 30 mV at stationary electrodes.

![Graph](image-url)  
**Fig. 4** Typical SWASV results at the wall-jet electrode for Cd ([Cd\(^{2+}\)] = 1.00 \times 10^{-7}\) mol l\(^{-1}\), Pb ([Pb\(^{2+}\)] = 1.00 \times 10^{-7}\) mol l\(^{-1}\), and a mixture of Cd and Pb ([Cd\(^{2+}\)] = [Pb\(^{2+}\)] = 1.00 \times 10^{-7}\) mol l\(^{-1}\)). Other conditions: \(f = 100\) Hz; \(h = 50\) mV; and \(t_{dep} = 120\) s.

![Graph](image-url)  
**Fig. 5** Variation of peak current with flow rate for SWASV at a wall-jet electrode, illustrated for Pb ([Pb\(^{2+}\)] = 5.00 \times 10^{-8}\) mol l\(^{-1}\)). Other conditions as in Fig. 4.
Plots of peak current versus deposition time for Cd and Pb are shown in Fig. 6; these are linear for deposition times up to 250 s, with close-to-zero intercepts. For high deposition times, some curvature in the plots is evident.

Calibration graphs for (a) the two metal ions and (b) their mixture are shown in Fig. 7. Good reproducibility and repeatability were encountered: at 10 nmol l\(^{-1}\), and for the square-wave parameters used to collect the data in Fig. 7, the peak current relative standard deviations (s\(_r\)) were 2.5 and 1.5% for five determinations, separately or in a mixture, respectively. The slopes of these plots are 5.2 and 3.2 A mmol\(^{-1}\) l\(^{-1}\) for cadmium and lead, respectively, when analysed separately, and 6.6 and 2.9 A mmol\(^{-1}\) l\(^{-1}\), respectively, in the mixture. In contrast to stationary-electrode experiments, the cadmium sensitivity increases in the mixture, and that of lead decreases slightly. Although it is not clear at present why this happens, the explanation advanced in the previous section for the peak current in mixtures at stationary electrodes will be much more sensitive to any electrode kinetic effects. Hence, owing to the interplay of mass transport and kinetics, although lead gives larger peak currents than cadmium at stationary electrodes, at wall-jet electrodes the opposite is true: in this instance, we recall that the square-wave peak is effectively the differential of the I versus E curve.

From the slopes of the calibration graphs, a much greater sensitivity is seen at wall-jet electrodes than at stationary electrodes. The effect of not performing the stripping step in de-oxygenated solution leads to slightly lower precision, but this is outweighed by the simplifications in the experimental procedure and configuration. Taking into account the different deposition times, it is found that the sensitivity is much higher than for experiments under optimized conditions at stationary electrodes. From the noise level, a detection limit of \(10^{-10}\) mol l\(^{-1}\) can be estimated for the method using stationary electrodes.

**Comparison Between Stationary and Wall-jet Electrodes**

The advantages of wall-jet electrodes in continuous-flow systems, where there is no depletion of the incoming reagent which impinges on the electrode, and on-line monitoring is possible, were stressed earlier. The enhanced mass transport with respect to a stationary electrode in stirred solution also leads to higher sensitivities. Both phenomena lead to reproducible results. However, the extra sensitivity obtained at the wall-jet electrode coupled with a slightly improved reproducibility (s\(_r\) = 2.5%, as opposed to 3.0% for five determinations at 10 nmol l\(^{-1}\)) leads to a decrease in the practical detection limit by about one order of magnitude down to nanomolar concentrations.

As seen earlier, the optimum conditions for the operation of the SWASV experiment are different at stationary and wall-jet electrodes. These differences can be understood by consideration of the concentration-gradient profile during the stripping step. The wall-jet electrode will be much more sensitive to any electrode kinetic effects. Hence, owing to the interplay of mass transport and kinetics, although lead gives larger peak currents than cadmium at stationary electrodes, at wall-jet electrodes the opposite is true: in this instance, we recall that the square-wave peak is effectively the differential of the I versus E curve.

Future work will address the problem of extending the use of SWASV at wall-jet electrodes to more complex mixtures of metal ions, in order to lead to a versatile, on-line sensor.

**Conclusions**

This work has demonstrated the viability of performing SWASV of lead and cadmium at concentrations down to nanomolar levels in non-de-oxygenated solution with good reproducibility. Optimum conditions with respect to deposition time, square-wave frequency, and amplitude have been determined.

The sensitivity is higher at wall-jet than at stationary electrodes, and detection limits are lower. Coupled with the advantages of on-line continuous-flow systems, this means that wall-jet electrodes are to be preferred to stationary electrodes. This method should be readily applicable to the determination of other trace metal ions.

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**References**


