

## THE WALL-JET RING-DISC ELECTRODE

### PART II. COLLECTION EFFICIENCY, TITRATION CURVES AND ANODIC STRIPPING VOLTAMMETRY

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#### ABSTRACT

Experimental results are reported using the wall-jet ring-disc electrode for the limiting currents on the disc and on the ring, for the collection efficiency for diffusion layer titration curves and for anodic stripping voltammetry with collection. In all cases experiment and theory are found to be in reasonable agreement. It is also shown that when electroactive substances are injected into the wall-jet chamber they cause no current on the disc or ring electrode thereby proving that the electrodes always are in contact with fresh solution which has just come through the jet. Results for the effect of varying the jet nozzle electrode distance are presented and discussed.

#### INTRODUCTION

In Part I of this series [1] we presented the theory of the wall-jet ring-disc electrode (WJRDE). In this paper we report experimental investigations using this electrode. We report results for the collection efficiency for diffusion layer titration curves and for anodic stripping voltammetry with collection. In this last technique the target metal is plated on the disc, but the stripping current is not measured on the disc. Instead the ring is used to collect the metal as it is stripped off. This avoids problems from spurious disc currents associated with double layer charging or with oxidation of the disc electrode surface. The technique has been hitherto on a rotating ring-disc electrode [2] and on a tube double electrode [3].

Before describing the ring-disc studies we report results of a "non-collection" experiment. As described in our previous paper [1], while the velocity of the solution in the direction normal to the electrode,  $v$ , is towards the electrode at large distances, close to the electrode surface the flow is *away* from the electrode. The flow is zero along the surface given by:

$$\eta = 0.51k(V_t/v)^{3/4} a^{-1/2} r^{-5/4} z = 3.96 \quad (1)$$

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where  $V_f$  is the volume flow rate through the jet;  $\nu$  is the kinematic viscosity;  $a$  is the nozzle diameter;  $r$  is the radial distance;  $z$  is the distance normal to the electrode;  $k = 0.86$  [4].

This means that dead solution in the chamber of the wall-jet electrode does not reach the electrode surface; only fresh solution that has just come through the jet can get inside the surface given by eqn. (1). We have tested this prediction by electrogenerating  $\text{Fe}(\text{CN})_6^{3-}$  in the chamber on an auxiliary electrode. We have also explored the effects of varying the distance between the nozzle of the jet and the electrode.

## EXPERIMENTAL

Two wall-jet cells of the type developed by Fleet [5] were used in this work; the design is shown in Fig. 1. The first was used to test the theoretical equations derived above and the second smaller version used for anodic stripping voltammetry experiments. The electrodes were made of platinum and were polished with  $6\ \mu\text{m}$  and  $3\ \mu\text{m}$  diamond lapping compound on a polishing table, and then by hand with  $1\ \mu\text{m}$  alumina made into a slurry with double distilled water. Between experiments they were polished by hand with  $0.3\ \mu\text{m}$  alumina slurry to ensure reproducibility of results. The radii were measured with a travelling microscope and were:

Cell A:  $r_1 = 3.499\ \text{mm}$ ,  $r_2 = 3.738\ \text{mm}$ ,  $r_3 = 3.999\ \text{mm}$ .

Cell B:  $r_1 = 1.654\ \text{mm}$ ,  $r_2 = 1.759\ \text{mm}$ ,  $r_3 = 1.885\ \text{mm}$ .

The respective nozzle diameters were  $0.34\ \text{mm}$  and  $0.41\ \text{mm}$ . The solution was driven

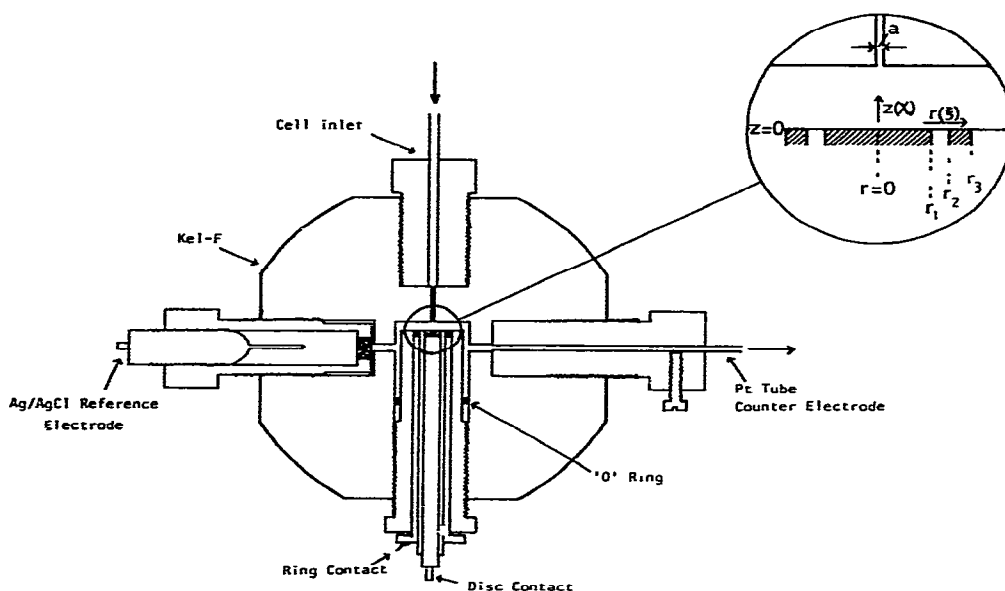


Fig. 1. The wall-jet cell with the notation used in this work.

through the jet by a Pharmacia P-3 three channel peristaltic pump. A hollow glass ball and 5 m length of Teflon tubing were used to minimise pump pulsations. The sucking mode with the pump downstream of the outlet was used when deoxygenation was required (ASV experiments). Flow-rates were calibrated volumetrically each day and all experiments were conducted at room temperature.

All chemicals used were of AnalaR grade or equivalent and were made into solution with deionised, doubly distilled water. For ASV experiments it was found necessary to pre-electrolyse the potassium sulphate supporting electrolyte and this was achieved by applying a suitable potential between two large Pt gauze electrodes immersed in the stirred solution in a glass vessel. 24 h was enough to remove the impurities to a sufficiently low level. Deoxygenation was achieved by passing oxy-free nitrogen through two Dreschel bottles containing Na-9,10-anthraquinone-2-sulphonate/zinc amalgam in sodium hydroxide solution, then through supporting electrolyte and finally into the solution reservoir (500 ml, conical flask). Nitrogen was bubbled for 20 min prior to and during experiments.

Diffusion coefficients were measured at the RRDE and had the following values:

$$D_{298}(\text{Fe}(\text{CN})_6^{4-}) \text{ in } 0.4 \text{ M } \text{K}_2\text{SO}_4 = 5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

$$D_{298}(\text{Br}^-) \text{ in } 0.5 \text{ M } \text{H}_2\text{SO}_4 = 9.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

Viscosities were measured using an Ostwald viscometer and were

$$\nu_{298}(0.4 \text{ M } \text{K}_2\text{SO}_4) = 9.41 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$$

$$\nu_{298}(0.5 \text{ M } \text{H}_2\text{SO}_4) = 9.51 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$$

Since the experiments were conducted at room temperature (usually 294 K or 295 K) a correction factor for  $D$  of  $1\frac{1}{2}\%/K$  was made.

## RESULTS AND DISCUSSION

### *The "non-collection" experiment*

As discussed above, the theoretically derived wall-jet velocity profile predicts that the fluid velocity component perpendicular to the electrode,  $v$ , is directed away from the electrode at the electrode surface for all  $r$ . This implies that the electrodes always receive fresh solution from the impinging jet and not from recirculation of the solution already within the cell. It was decided to check this experimentally.

A platinum wire was inserted through a small hole drilled through the side of the cell body of Cell A with  $\sim 1.5$  cm protruding into the cell. It was Araldited into place and aligned so as to lie along the back wall, its tip just short of the nozzle. Using a solution of  $10^{-2}$  M  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.4 M  $\text{K}_2\text{SO}_4$  supporting electrolyte the wire was potentiostatted at +0.5 V vs. SCE to generate ferricyanide and the disc and ring potentiostatted at 0.0 V to reverse the reaction should any ferricyanide reach them. The disc/ring current was monitored, and on stepping the wire potential from 0 V to +0.5 V no change was detected (limit of detection 1 nA). It should be

noted that for this solution and the flow rates used ( $0.015 \rightarrow 0.125 \text{ cm}^3 \text{ s}^{-1}$ ) the diffusion-limited currents at the disc/ring electrodes are of the order of 1 mA. Different positions of the wire within the cell and nozzle/electrode separation were tested and in all cases there was zero response.

We may therefore conclude that the disc and ring electrodes do always receive fresh solution direct from the jet.

#### INFLUENCE OF NOZZLE/ELECTRODE SEPARATION

Results obtained by varying the nozzle/electrode separation, keeping the flow-rate constant for  $i_{D,L}$ ,  $i_{R,L}$  and  $N_0$  are shown in Fig. 2. The reaction studied was the oxidation of 3 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.4 M  $\text{K}_2\text{SO}_4$  supporting electrolyte. Values at

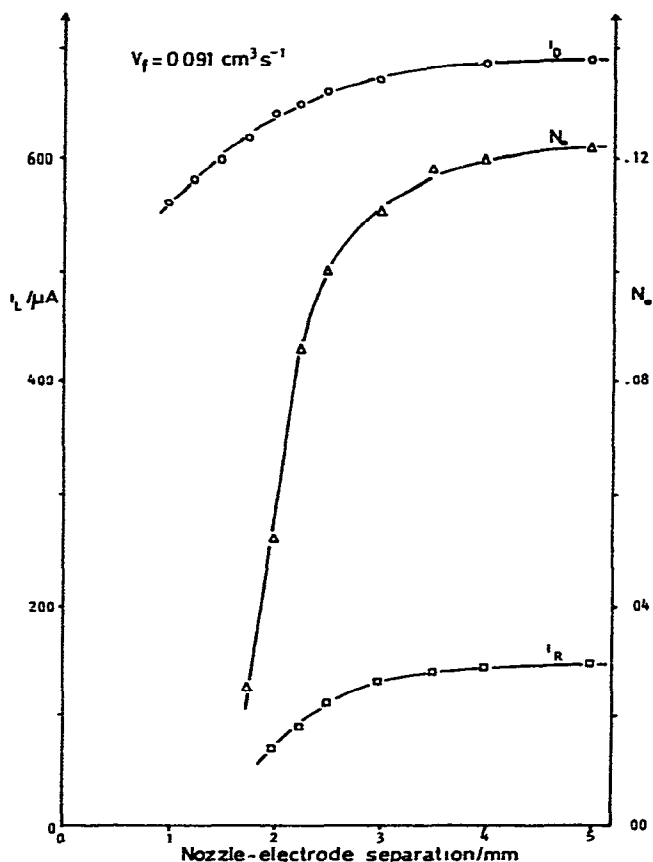


Fig. 2. Effect on the limiting disc current, the limiting ring current and the collection efficiency of varying the separation of the jet nozzle and the electrode.

large separation correspond to those predicted. The collection efficiency reaches its predicted value only at the same separation as the limiting ring current.

We may explain these results by examining the flow functions and streamlines in Part I [1].

As the radius  $r$  increases the hydrodynamic boundary layer becomes thicker and the back wall containing the nozzle will interfere with the flow. This is the reason why the ring electrode current (and  $N_0$ ) require a greater nozzle-electrode separation than the disc electrode. The fact that at large values of  $z$  there is a steady flow of solution towards the electrode means that there must be an inward radial flow of solution along the back wall. When the separation gets too small this inward flow interferes with the outward flow pattern across the electrode surface. Where  $v$  is towards the electrode it is reduced while close to the electrode surface it will be increased. The boundary given by eqn. (1) will be shifted outwards from the electrode and so less material will reach the ring electrode.

The conclusion, therefore, is that the back wall/electrode separation rather than the nozzle/electrode separation is the relevant factor. In Cell A the maximum possible separation is 5 mm and so, subsequent experiments were all performed at this distance.

#### VOLTAMMOGRAMS AND COLLECTION EFFICIENCIES

Voltammograms at disc and ring electrodes were recorded for oxidation of 3 mM  $K_4Fe(CN)_6$  with 0.4 M  $K_2SO_4$  supporting electrolyte. Fig. 3 shows typical voltammograms obtained and plots of  $i_L$  vs  $V_f^{3/4}$ . In Table 1 we present the slopes of these plots and collection efficiencies together with  $\beta^{2/3}$ , obtained experimentally and predicted theoretically. Reasonable agreement is found. The slope of the disc plot is as expected but that for the ring is a little large leading to a somewhat higher value of  $\beta^{2/3}$  than that predicted. The experimental collection efficiency is also somewhat higher than predicted. It was satisfactory that it was independent of flow rate. The reasons for the small discrepancies between the theoretical predictions and experimental results in Table 1 are unclear. Possible reasons are interference with the flow

TABLE 1  
Results for wall-jet ring-disc electrodes

	$i_{D,L} V_f^{-3/4} /$ mA (cm <sup>3</sup> s <sup>-1</sup> ) <sup>-3/4</sup>	$i_{R,L} V_f^{-3/4} /$ mA (cm <sup>3</sup> s <sup>-1</sup> ) <sup>-3/4</sup>	$\beta^{2/3}$	$N_0$
<b>3 mM <math>K_4Fe(CN)_6</math></b>				
Theoretical	2.20 ± 0.15	0.44 ± 0.03	0.20	0.118
Experimental	2.19 ± 0.03	0.50 ± 0.02	0.23	0.123
<b>3 mM KBr</b>				
Theoretical	4.3 ± 0.3	0.85 ± 0.06	0.20	0.118
Experimental	3.4 ± 0.1	0.78 ± 0.02	0.23	0.140

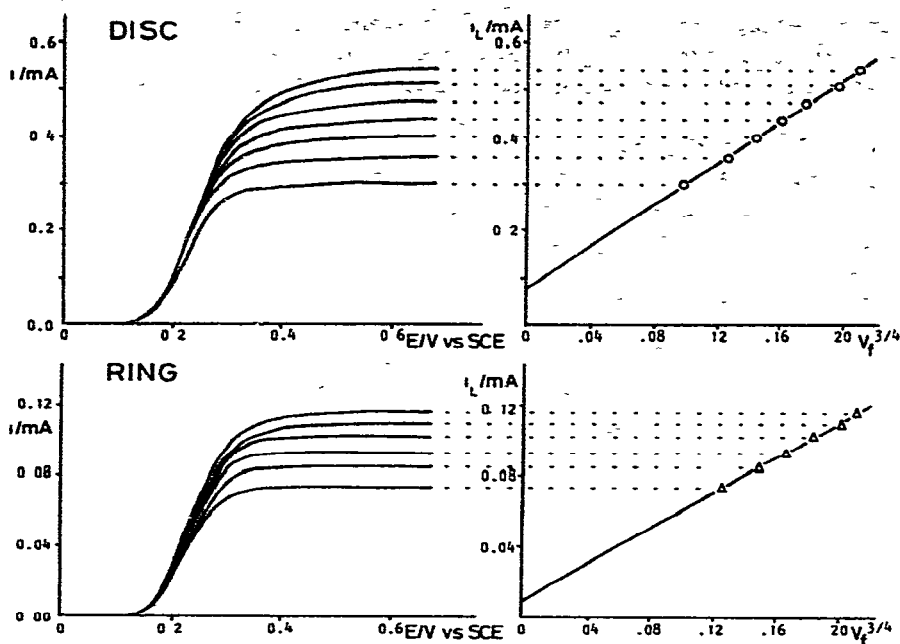


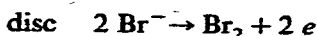
Fig. 3. Typical current-voltage curves on the ring and disc electrodes showing variation of the limiting current with (flow rate)<sup>3/4</sup>.

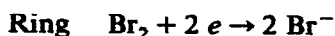
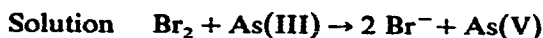
pattern from the back wall or the jet may not be exactly in the centre of the disc. The radii of the wall-jet ring disc electrode are smaller than the typical radii for the rotating ring-disc electrode so any geometric misalignment will be more serious.

Similar experiments were undertaken for the oxidation of 3 mM KBr in 0.5 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte and the results are also presented in Table 1. The agreement here is again fairly reasonable but rather less good than for the Fe(CN)<sub>6</sub> system. In particular it is not clear at this stage why the value of  $N_0$  is significantly larger than that predicted. Experiments with both systems on a rotating ring-disc electrode gave the same value of  $N_0$  in good agreement with the theoretical value. It may be that the Br<sup>-</sup> system is not sufficiently reversible to give the required current distribution on the wall-jet disc electrode. This would result, for a given current, in more Br<sub>2</sub> being generated on the outside edge of the disc and less at the centre, giving a higher collection efficiency.

#### DIFFUSION LAYER TITRATIONS

Results were obtained for the system





The bromide was present in excess as  $10^{-2} M$  KBr in  $0.5 M$   $\text{H}_2\text{SO}_4$  supporting electrolyte, and the As(III) was dissolved in  $0.5 M$   $\text{H}_2\text{SO}_4$ . The ring potential was held at  $+0.45 V$  vs. SCE to reduce the bromide reaching it. A range of arsenic(III) concentrations from  $10$  to  $100 \mu\text{mol dm}^{-3}$  was studied. Fig. 4 shows typical titration curves.

In our previous paper [1] we showed (eqn. (35)) that:

$$N'_{\beta, -\beta} = 1 - F\left(\frac{\alpha}{\beta}\right) - \frac{1 + \alpha}{(1 + \alpha + \beta)^{1/3}} \left[ 1 - F\left\{\frac{(1 + \alpha + \beta)\alpha}{\beta}\right\} \right]$$

where:

$$\alpha = (r_2/r_1)^{9/8} - 1$$

$$\beta = (r_3/r_1)^{9/8} - (r_2/r_1)^{9/8}$$

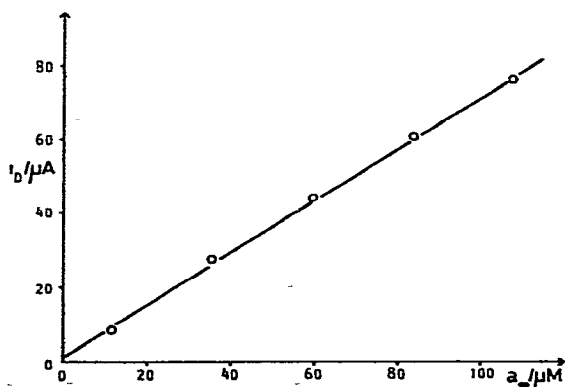
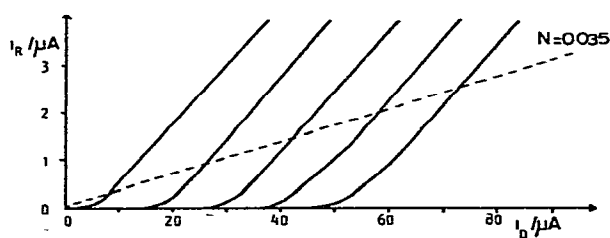


Fig. 4. Typical titration curves for the reaction between  $\text{Br}_2$  and As(III) for varying concentrations of As(III),  $a_\infty$ . The lower graph shows that the disc currents found at  $N' = 0.035$  vary linearly with  $a_\infty$ , as required by eqns. (4) and (5).

and

$$F(\theta) = \frac{3^{1/2}}{4\pi} \ln \left\{ \frac{(1 + \theta^{1/3})^3}{1 + \theta} \right\} + \frac{3}{2\pi} \tan^{-1} \left( \frac{2\theta^{1/3} - 1}{3^{1/2}} \right) + \frac{1}{4}$$

For the electrode of cell A

$$N'_{\beta_1 = \beta} = 0.0135$$

For disc currents greater than those given by the intersection of  $N'_{\beta_1 = \beta}$  with the titration curve, the ring electrode is entirely inside the bromide dominated zone and the linear relation given in eqn. (34) of ref. 1 holds:

$$|i_R| = N_0 |i_D| - \beta^{2/3} |i_{As}| \quad (2)$$

where  $N_0$  is the collection efficiency and  $i_{As}$  is the limiting current that would be observed on the disc electrode if the As(III) was electroactive. In order to avoid any kinetic effects caused by the finite rate of reaction between  $Br_2$  and As(III), we have carried out the analysis using  $N' = 0.035$ , a value which is significantly larger than the critical value of 0.0135. We can therefore be certain that eqn. (2) holds. Since

$$|i_R| = N' |i_D| \quad (3)$$

we can eliminate  $|i_R|$  between eqns. (2) and (3) and rearrange to obtain

$$|i_D|_N = \beta^{2/3} (N_0 - N')^{-1} i_{As} \quad (4)$$

where [1]:

$$i_{As} = 1.60k_2 F D^{2/3} \nu^{-5/12} V_f^{3/4} a^{-1/2} r_1^{3/4} [As(III)] \quad (5)$$

Plots of  $|i_D|_N$  against  $[As(III)]$  we found to be linear; a typical example is shown in Fig. 4. From the gradients of these plots and from eqns (4) and (5) we can calculate values for  $D$  where we have used the values of  $N_0$  and  $\beta$  reported in Table 1. The average value of  $D$  is  $0.96 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and is in good agreement with the value of  $D$  of  $0.98 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , found for bromide arsenic titrations using the rotating ring-disc electrode [6]. Hence we may conclude that ring-disc titrations can be carried out on the wall-jet system and that theory and experiment are in reasonable agreement. The advantage of the wall-jet system is that it has no moving parts and very little dead space. This makes it an ideal cell for coupling to a chromatographic column. A subsequent paper will describe the use of the electrode as a general detector for proteins using the bromide titration method [7].

#### ANODIC STRIPPING VOLTAMMETRY WITH COLLECTION (ASVWC)

The technique of ASVWC was originally developed for the RRDE [2]. It discriminates against the capacitive current in the stripping step by monitoring the ring current resulting from potential step stripping of the disc: the ring is kept at a constant potential. Integration of the ring transient determines the charge stripped from the disc and thence the concentration of electroactive species under study.



Unlike most ASV techniques for detecting low concentrations, sophisticated instrumentation is not required.

Before applying this technique to the WJRDE we first need to consider whether for a double electrode with non-uniform deposition the fraction of stripped species reaching the ring is indeed  $N_0$  (as it is for the RRDE).

Consider a small radial element of the disc of width  $\delta r$ . On stripping, a fraction  $N'(r)$  of the material from this element will reach the ring electrode and the remainder will be lost. Hence the amount of material (expressed as charge) which is recovered on the ring is given by:

$$|q_R| = \int_0^{r_1} N'(r) |q'(r)| dr \quad (6)$$

where  $q'(r)$  describes the distribution of material from plating on the disc electrode. Now

$$q'(r) = t_{dep} t'_D(r) \quad (7)$$

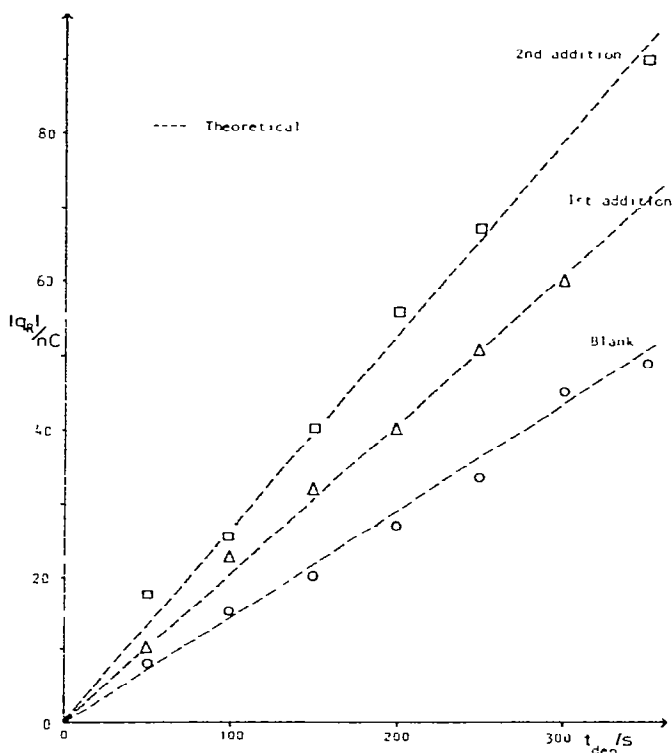


Fig 5 Typical results for ASVWC experiments for Cu(II) in  $0.4 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$ , plotted according to eqn (10). Each addition consisted of the galvanostatic injection of  $10 \text{ nmol dm}^{-3} \text{ Cu(II)}$ .

where  $t_{\text{dep}}$  is the deposition time and  $i'_D(r)$  is the radial current distribution on the disc for the limiting current. Now in an ordinary collection experiment:

$$N_0 = \int_0^{r_1} N'(r) i'_D(r) dr / \int_0^{r_1} i'_D(r) dr \quad (8)$$

Substitution of eqns. (7) and (8) in eqn. (9) gives the simple result:

$$|q_R| = N_0 t_{\text{dep}} |i_D| = N_0 |q_D| \quad (10)$$

The deposition of the metal according to the limiting current distribution means that the correct boundary condition for  $N_0$  is achieved during the stripping operation.

The technique of ASVWC was tested using the smaller wall-jet cell. This was because with the larger cell the transit time for the stripped material to reach the ring electrode was too long being about 0.3 s. The smaller cell had a transit time of about 0.05 s which is comparable to that of an RRDE. Typical results for the determination of copper in  $0.4 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$  are displayed in Fig. 5. The copper concentration in the test solution was increased by electrochemical injection of  $10 \text{ nmol dm}^{-3}$  of Cu(II) using a galvanostat and a small copper wire. It can be seen that the technique provides a reliable method for estimating copper at concentrations of the order of  $10^{-8} \text{ mol dm}^{-3}$ . Despite pre-electrolysis the copper level in our blank was still rather high. If this were reduced we anticipate that trace levels down to  $10^{-10} \text{ mol dm}^{-3}$  could be measured. Again the advantage of the wall-jet configuration is that it is an ideal on line sensor.

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