

TRACE METAL ANALYSIS AT THE WALL-JET RING-DISC ELECTRODE

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Electrochemical on-line sensors are particularly useful for the determination of many chemical species present at trace level in aqueous solution, not only for pollution and process control, but also for monitoring and optimising trace element levels in biological situations. Response is rapid, the hydrodynamic characteristics[1] as well as regular calibration ensure good reproducibility and accuracy, and automation signifies a minimum of assistance.

We have been developing a wall-jet ring-disc electrode amperometric flow-through sensor for the determination of trace metals using the double electrode technique of stripping voltammetry with collection (SVWC)[2]. In this technique[3] the species of interest is preconcentrated by electrodeposition onto the disc electrode for time t_{dep} , and then stripped by a step change in applied potential, a fraction N_c (the steady-state collection efficiency) being collected at the ring electrode, whose potential is equal to the disc deposition potential. The charge passed at the ring, q_R , gives the analyte concentration directly according to the formula

$$q_R = -N_c i_D t_{dep}$$

i_D , the disc current during the preconcentration step, being proportional to concentration. The design of the wall-jet cell has been described elsewhere[4].

We have previously applied the technique, using a glassy carbon - platinum ring-disc electrode to the determination of copper, manganese and nickel at the submicromolar level[2]. In order to determine zinc and other cations deposited as the metal, it is necessary to extend the negative potential range available. This can be achieved by the use of mercury thin-film electrodes obtained by *in situ* plating of glassy carbon. This work therefore employs a glassy carbon - glassy carbon ring-disc electrode.

For anodic stripping voltammetric determinations, therefore, the added electrolyte - sodium perchlorate 0.1 mol dm^{-3} - was spiked with $5 \times 10^{-5} \text{ mol dm}^{-3}$ mercury(II). In this way copper, zinc and manganese at submicromolar level were determined by reduction to the metal, being codeposited with the mercury. Manganese was also estimated by oxidation to manganese dioxide on the disc electrode and subsequent cathodic stripping. The potentials employed for the various determinations are shown in Table 1, and an example of results obtained in Fig.1. Calibration was carried out by the standard addition method. In all cases experiment was in good agreement with wall-jet electrode theory.

Table 1. Deposition and stripping potentials employed for SVWC

Species deposited	Deposition potential /V vs Ag/AgCl	Stripping potential /V vs Ag/AgCl
Cu ^a	-0.50	+0.10
Zn ^a	-1.25	-0.95
Mn ^a	-1.75	-1.35
MnO ₂ ^b	+0.75	0.00

^a Electrolyte 0.1M NaClO_4

^b Electrolyte $0.1 \text{M KCl/borate buffer pH 7.2}$

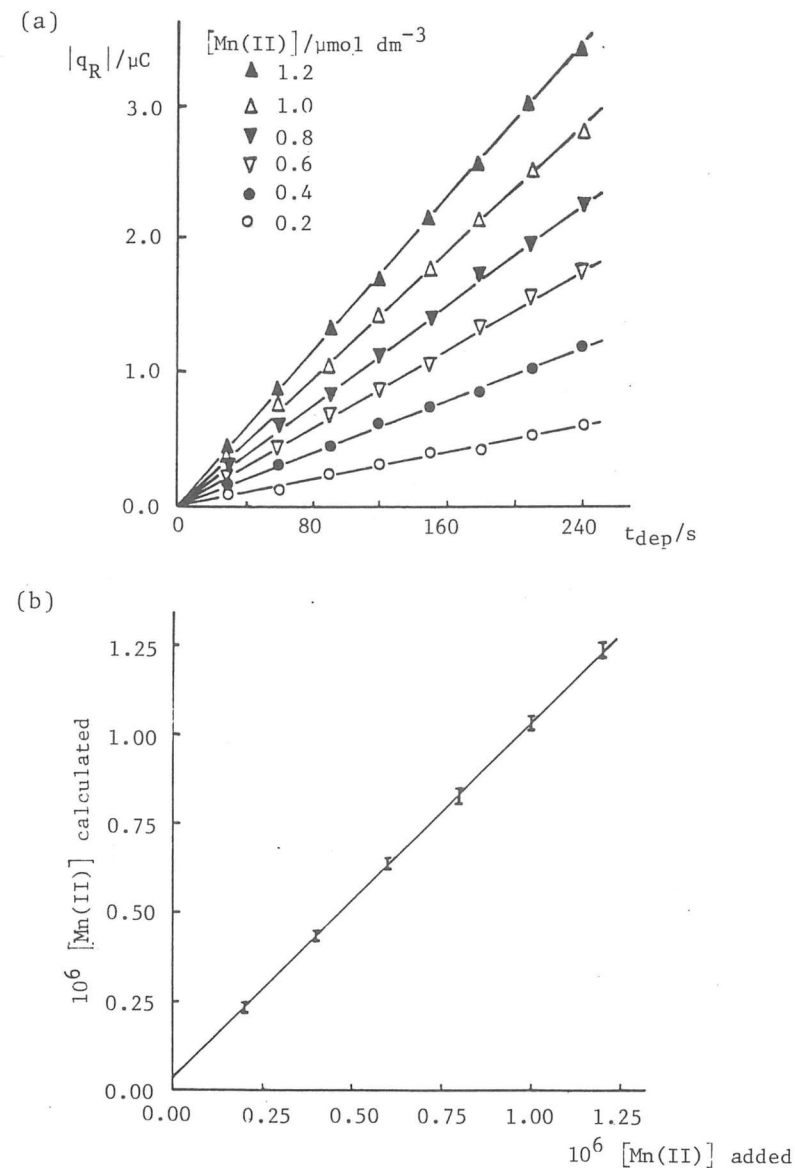


Fig.1 Cathodic SVWC of manganese(II) at wall-jet ring-disc electrode; experimental conditions as in Table 1.

(a) Calibration plot using standard addition method;

(b) $[\text{Mn(II)}]$ calculated from experiment vs. $[\text{Mn(II)}]$ added.

In the determination of copper, zinc and manganese in the same solution there is intermetallic compound formation between copper and zinc in the mercury thin-film electrode; the stripping potential of Cu-Zn is almost coincident with that of copper. In order to overcome this we determine copper alone (deposition at $-0.5V$), and then deposit zinc and copper together (deposition at $-1.25V$): simple subtraction of the copper concentration from the copper plus zinc value gives the zinc concentration. In addition to regular stripping of the mercury film from the disc electrode, this was found to give reliable and accurate results.

An important advantage is that the same wall-jet sensor can be used for copper, zinc and manganese present in the same solution. We have applied it to the analysis of these trace elements in nutrient solutions for hydroponic cultures. No interferences from other species present in the nutrient solution were found.

References

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DIELECTRIC PROPERTIES OF BINARY MIXTURES OF CYCLOHEXANOL AND NON-POLAR LIQUIDS

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INTRODUCTION

Data on dielectric properties of cyclohexanol are scarce and those available quoted from rather old sources. As we need the values for the dielectric constant and electrical dipole moment for this compound some work has been done in order to determine these properties.

In this paper results for the static dielectric constant of cyclohexanol at temperatures between 12 and 35°C and of binary mixtures of this compound with cyclohexane and carbon tetrachloride at 25°C are presented. From these results it is possible to determine the electrical dipole moment of the polar component. The reason for using two non-polar solvents is to see to what extent the non-polar component plays any role in the value obtained for the dipole moment.

EXPERIMENTAL

The dielectric properties have been measured with a Sargent oscilloscope whose features have been described in another paper presented