

SOLIOMETRY—A NEW ELECTROANALYTICAL TECHNIQUE

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SOLIONS, a family of liquid-state devices, are thin-layer redox cells in which the current is controlled by the diffusion of that component of the redox couple present in a relatively small concentration¹. A typical example is the iodine-iodide solion fabricated with two closely spaced, plane parallel, inert electrodes of equal area. (The iodine, actually tri-iodide I_3^- concentration is usually in the millimolar range, and the iodide concentration in the molar range; further, the inter-electrode distance is between 10^{-3} to 10^{-1} cm). The steady-state current-potential curve of such a solion shows a characteristic diffusion-limiting current, I_1 , given by Fick's first law:

$$I_1 = \frac{2nFADC^\circ}{L}$$

where n is the number of electrons involved in the redox reaction ($n=2$ for $I_2 + 2e = 2I^-$, or $I_3^- + 2e = 3I^-$); A , the area of each electrode; D , the diffusion coefficient of the diffusing component, viz., $I_2(I_3^-)$ in the iodine-iodide solion; C° , the bulk concentration of this component, and L , the inter-electrode distance.

The linear variation of I_1 with C° in a solion does not seem to have been exploited hitherto for analytical purposes. However, by adding to the redox solution a species X which reacts stoichiometrically to generate or consume the diffusing component, the bulk concentration of the latter is altered to $C^\circ \pm \Delta C^\circ$, and as a consequence, the limiting current changes to $I_1 \pm \Delta I_1$. Hence, measurements of ΔI_1 permit² the estimation of the species X through the relation

$$\Delta I_1 = \left(\frac{2nFDA}{L} \right) \left(\frac{\nu}{M} \right) C_x$$

where ΔI_1 is in μA , C_x is the concentration of the species X in $\mu g\ cm^{-3}$, i.e., in ppm, and ν is the number of moles of the species X (of formula weight M) reacting with one mole of O to produce R , or with one mole of R to produce O . The reaction between O/R and X need not be of the oxidation-reduction type; if it is, then $\nu = n'/n$ where n' is the number of electrons involved in the

transformation ($O' + n'e = R'$) of the oxidized (O') and reduced (R) forms of the species X .

The new technique being proposed here may be called *solimetry* rather than *thin-layer amperometry with amperometric indicator* because the former term stresses the utilization of solion devices for analysis, whereas the latter relates the technique to other methods of electro-analysis.

An idea of the sensitivity S accessible to solimetry can be gained by writing

$$S = (\Delta I_1/C_x) = 2FD \left(\frac{A}{L} \right) \left(\frac{n'}{M} \right)$$

and by noting that if $FD \approx 1\ \mu A\ \mu mole^{-1}\ cm^2$, $n' = 1$ and $M = 100$, then

$$S = 2 \times 10^{-2} (A/L)\ \mu A/ppm.$$

The (A/L) ratio depends on the apparatus used. If the plane parallel electrodes are mounted on the anvil and shaft of a micrometer, one can easily achieve an (A/L) ratio of 10^3 corresponding to $A = 10\ cm^2$ and $L = 10^{-2}\ cm$ in which case $S = 20\ \mu A/ppm$. Thus, hundredths of a ppm of X can be determined if the changes in the solion limiting current are read to an accuracy of 0.2 A. This analysis of concentrations at the 10^{-7} molar level requires a solution volume of $AL = 10^{-1}\ cm^3$ only. It has been claimed³ that the closest inter-electrode distance conveniently attainable is of the order of $10^{-3}\ cm$ which means that analysis at the 10^{-2} ppm (10^{-7} molar level) can be achieved with $10^{-3}\ cm^3$ of solution. Thus, *solimetry permits trace analysis of microquantities of solution*. An added feature is the easy adjustment of sensitivity by a variation of the inter-electrode distance.

With the aid of solions based on iodine-iodide, cerous-ceric, vanadous-vanadic, etc., couples, the solimetric technique can be adapted to analyses based on iodimetry, cerimetry, vanadimetry, etc.. There are two restrictions on the species X to be estimated: (1) it must react quantitatively with one of the compounds O and R of the solion redox couple; (2) the reaction by which the species X

produces or consumes the diffusing component of the solion must be fast enough to produce a time-independent limiting current. If however X undergoes a slow reaction with a component of the solion couple, then the time variation of the limiting current can be used to study the kinetics of the reaction⁴.

The theory of interference is similar to that in potentiometric titrations. Thus, if $E^\circ_{O/R}$ is the standard electrode potential for the redox couple of the solion and $E^\circ_{O''/R''}$ is that for the oxidized and reduced forms of another species Y present along with the species X to be determined, then R'' will interfere if $E^\circ_{O''/R''} < E^\circ_{O/R}$, and O'' will interfere if $E^\circ_{O''/R''} > E^\circ_{O/R}$.

tin (II), ferrocyanide, antimony (III), thiosulphate, hydrogen peroxide, iodate, dichromate and perosulphate.

The apparatus consisted of two platinum-coated microscope slides held with Araldite to the anvil and shaft of a micrometer (of least count 0.01 mm). The micrometer assembly was attached to a laboratory stand so that the microscope-slide electrodes could be lowered into a beaker containing the mixture of the solion electrolyte and the species X being determined. Using a microammeter to read the changes in solion limiting current and a 1.5 V Leclanche cell to polarize the iodine-iodide solion to about 0.2 volts (oxygen interference commences around 0.5 volts), determinations at the ppm level have been easily achieved even with this set-up, as may be seen by the results⁵ on the determination of sulphur dioxide in the manganese bath (Fig. 1).

Soliometry has recommended itself therefore as an extremely simple, inexpensive and elegant technique of trace analysis. With minor changes of the electrode assembly and the coupling of two solions to achieve compensation of the temperature coefficient of the diffusion coefficient as well as a direct output of the difference ΔI_L , it appears that the technique can be refined to go down to the 10^{-2} ppm level with less than 10^{-2} cm³ of solution.

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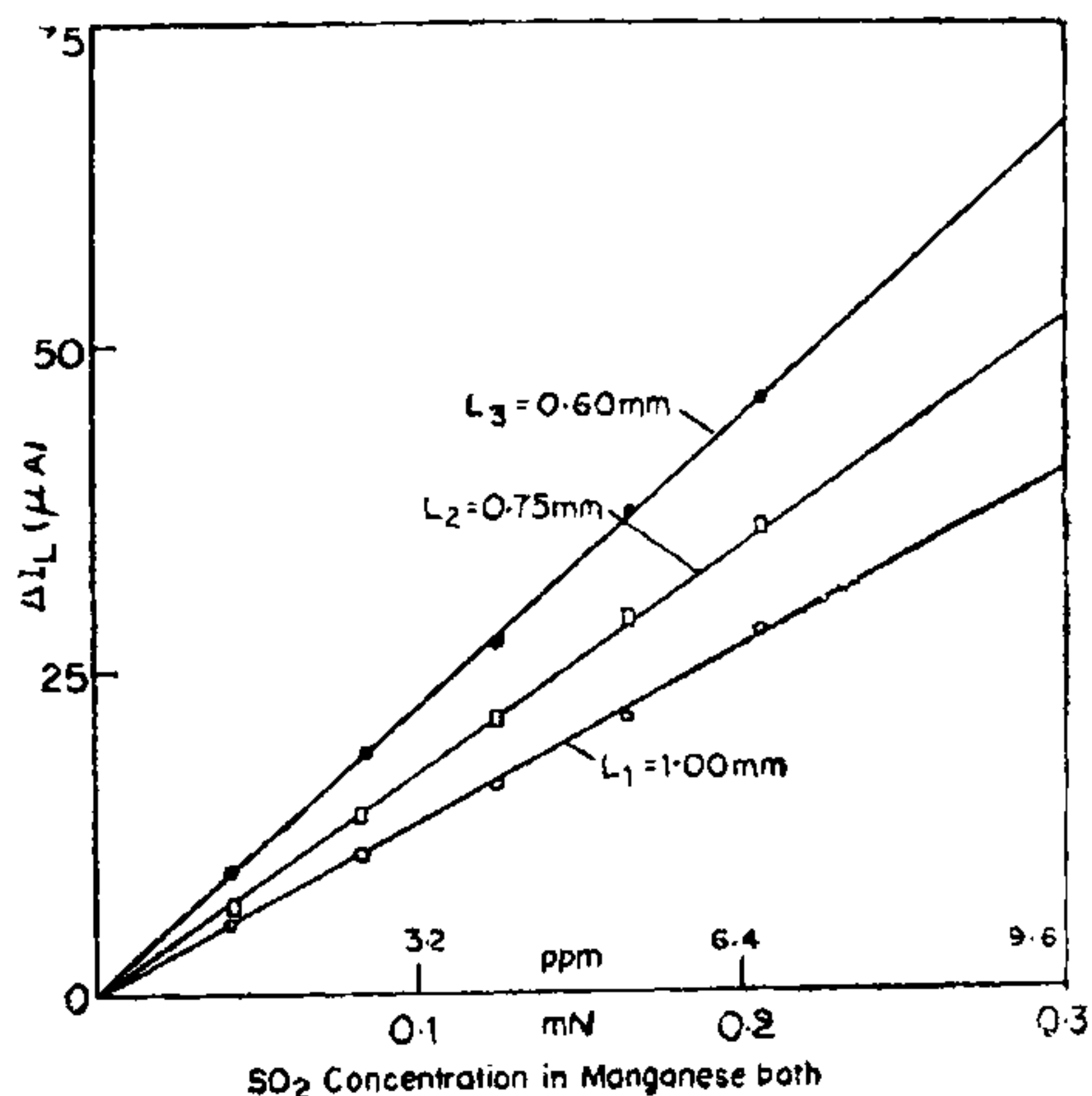


FIG. 1. Determination of SO₂ in manganese bath.

In collaboration with Gopal Reddy⁵, the solio-metric technique has been established for over a dozen estimations including amongst others the analysis of sulphite, sulphide, selenite, available chlorine in hypochlorite, copper (II) arsenic (III),