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## Trace Determination of Oxygen by a Potentiometric Method

By

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With 3 Figures

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The corrosion of amalgams can be regarded as a phase-exchange reaction between oxygen in a solution and the metal in the amalgam. It is known that traces of dissolved oxygen can be determined polarographically. This paper discusses the dependence of several factors in the corrosion of various amalgams on the concentration of oxygen, and its application to potentiometric determination of traces of oxygen in an inert gas.

### Experimental

A special cell was used, of the type described by Hartmann and Schölzel<sup>2</sup> (Fig. 1). The first two compartments of the cell contained pure mercury, and the third a heterogeneous amalgam of the metal being studied. All three compartments were then filled with a 0.1 M solution of a salt of the metal being studied. The cell was placed in an inert atmosphere in a plastic box, and hydrogen was passed through the system. The oxygen content in the atmosphere of the cell was determined by the Moogdan and Sixt method<sup>3</sup> after the system had reached equilibrium.

The amalgam in the third compartment was made the anode, and the mercury in the middle compartment the cathode of an electrolytic cell that was then used to generate a 0.01 M amalgam (0.01 mole of metal per litre of mercury) in the middle compartment, by constant-current electrolysis at 1 mA. The middle com-

partment was then suitable for use as a reference electrode. Then, under galvanostatic conditions, with a constant current of  $1\ \mu\text{A}$ , extremely dilute amalgams ( $10^{-4}$ — $10^{-7}\text{M}$ ) were produced in the

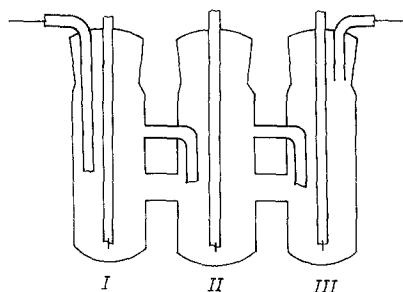


Fig. 1. Hartmann and Schölzel cell

first compartment, with amalgam in the third compartment as anode, and the pure mercury in the first compartment as cathode. The potential for each amalgam concentration was measured (against

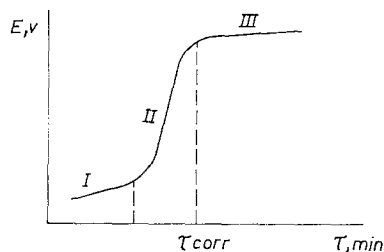


Fig. 2. Variation of potential with time in the oxidation of amalgams

the reference electrode) after the electrolysis. The change in potential ( $E$ , V) with time ( $\tau$ , min) was recorded with a recording potentiometer (type EPP 09).

As seen in Fig. 2, the resulting curves can be divided into three sections:

- (i) a very slow change in potential, associated with homogenisation of the amalgam after the electrolysis,
- (ii) a sudden change in the potential, connected with decomposition of the amalgam,
- (iii) a constant potential corresponding to that of pure mercury in presence of the electrolyte used.

These sections can be used for determination of the time needed for complete decomposition of the amalgam by the oxygen dissolved in the solution.

### Results and Discussion

For all the amalgams examined (Cu, Zn, Tl, Sn and Sb), the corrosion time is inversely proportional to the concentration of oxygen in the inert gas bubbled through the cell (Fig. 3). From this

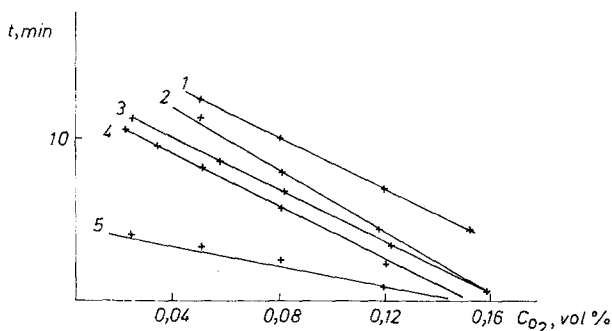


Fig. 3. Relation of oxidation time of amalgams to concentration of oxygen in the atmosphere. Amalgams  $1 \times 10^{-6}$  M. 1=Cu; 2=Sb; 3=Sn; 4=Tl; 5=Zn

figure it can be seen that the more electrochemically active the metal, the shorter the reaction time. From the data given it is seen that tin or antimony amalgam is the best for determining oxygen in gases in this way.

To determine oxygen contents  $>0.01\%$  v/v, it is necessary to use  $10^{-6}$  M amalgam but for  $<0.01\%$  oxygen,  $10^{-7}$  M amalgam must be used, but in that case only a copper amalgam is suitable, since the corrosion of a copper amalgam by oxygen is weaker than that of the other amalgams studied.

Hence  $0.001\%$  v/v oxygen in hydrogen can only be determined by using a copper amalgam. Further work has shown that there is also a definite relationship between the kinetic factors of the exchange process and the oxygen content, which allows analytical application of this system.

The corrosion rate constant is calculated from the relation between  $\log C/C_0$  and  $\tau$  (where  $C_0$  and  $C$  are the concentrations of the metal in the amalgam at time zero and time  $\tau$  respectively,  $\tau$  being the time of decomposition in minutes), on the supposition that the corrosion process is displacement of metal from the amalgam by the oxygen<sup>4</sup>. Research has shown that the corrosion process

appears to be a first-order reaction for both low ( $<0.01\%$  v/v) and high ( $>0.1\%$  v/v) oxygen concentrations.

We determined oxygen in chemically pure argon by using the time-dependence of the corrosion of dilute copper amalgams on the oxygen concentration in the cell atmosphere.

Argon, with unknown concentrations of oxygen, was passed through the cell and the time for complete decomposition of a copper amalgam ( $>10^{-6} M$ ) was used for determining the oxygen content in the atmosphere of the cell, by means of a calibration curve of time vs. log (oxygen content).

For higher oxygen concentrations thallium, zinc or tin amalgams are preferable.

### Summary

#### *Trace Determination of Oxygen by a Potentiometric Method*

A potentiometric method is proposed for the determination of microamounts of  $O_2$  in inert gases, based on the dependence of the corrosion time of dilute amalgams on the oxygen content in the atmosphere of the cell. The method was tested by analysis of chemically pure argon.

### Zusammenfassung

Eine potentiometrische Methode für die Bestimmung von Mikromengen Sauerstoff in inerten Gasen wurde vorgeschlagen, die auf der Abhängigkeit der Korrosionszeit verdünnter Amalgame von dem Sauerstoffgehalt der Atmosphäre in der Zelle beruht. Das Verfahren wurde an chemisch reinem Argon geprüft.

### References

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