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Amalgam Electrode Designed for Precise Electromotive Force Measurements

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In these decades a remarkable improvement has been achieved in ion selective electrodes. However, metal amalgam electrodes are still favorable for the precise electromotive force (emf) measurement of metal ions in solution because of their high accuracy and selectivity. The amalgam electrode may be disadvantageous in its handling and preparation and its instability caused by oxygen in air and dissolved in solution. Aladjoff's apparatus (1) is not suitable for storing the amalgam in the vessel after one has used it once. A usual J-type electrode described by Holloway and Reilley (2) is too simple in shape to prevent the contact of the amalgam phase with air during the preparation of the electrode. Therefore, from a practical point of view, an amalgam electrode which is easy to handle without lowering the precision is required by analytical chemists who are interested in the behavior of ions in solution.

The present electrode is designed on the basis of the following idea: a metal amalgam of a relatively low metal concentration is prepared by electrolysis of a solution containing relevant metal ions, and the amalgam is transferred to the tip of the electrode without contact with any stopcock or air. The apparatus depicted in Figure 1 consists of three parts, A, B, and C. A is the amalgam electrode which will be set in a measuring vessel. B is a chamber in which the metal amalgam is prepared by electrolysis in combination with a half-cell C. First of all, N_2 gas is introduced from *d* and the mercury is placed in the chamber *i* under the nitrogen atmosphere. The tip *c* is stoppered with a glass cap. The three-way stopcock *e* is turned so that N_2 gas flows from *d* to *i* through a guide tube *j*. A slightly acid solution containing metal ions is then introduced from *g* to *i*. The same solution is also poured from *n* into the half-cell C. The solutions in both compartments contact with each other at *k*, and *l* is closed with a pinchcock. During electrolysis of the solution by using a Pt foil as the anode and the mercury pool as the cathode (terminal *h*), N_2 gas is continuously bubbled from *d* to *m* and *m'* through *j*. When a desired amount of the metal amalgam is prepared, C is removed from B (this procedure is not absolutely necessary), and *g* is closed. The amalgam thus prepared can be stored for at least one month in this apparatus under a nitrogen atmosphere.

The electrode A is connected to an empty measuring vessel in which N_2 gas is filled. The gas streams from a gas inlet of the vessel to *a* (the cover is taken out) through the hole *b* and the tip *c*. *a* is then connected with *f* and the amalgam in B is transferred to *c* through *j* by pressing the mercury phase with N_2 gas. B can be removed from A, and a test solution is introduced to the measuring vessel.

When one makes amalgam from solid metal and mercury in B, part C is unnecessary to set.

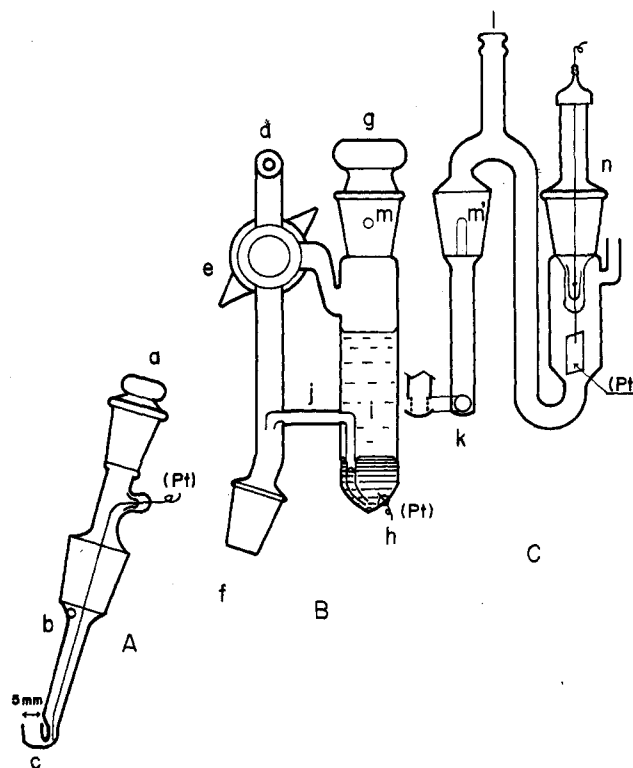


Figure 1. Amalgam electrode. Explanations of the symbols are given in the text

We used the electrode in combination with Kawai's reference half-cell (3) for measuring emf's of a cell containing Cd^{2+} , Pb^{2+} , or In^{3+} in ionic media of 1 M and 4 M $NaClO_4$. The measurements were carried out within ± 0.01 mV in each case. The potential reached a constant value within 10 min and remained unchanged for several hours at each point of the measurements.

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