Measurement of EMF of a cell

EMF of a cell can be determined by connecting a voltmeter between the electrodes. The voltage is read directly from the instrument. But the drawbacks of using this method are:

(1) The instrument draws current from the cell, causing a change in the emf due to formation of reaction produces at the electrodes and changes in the concentration of the electrolyte around the electrodes.
(2) An internal resistance of the cell is developed due to concentration polarization. Hence potentiometers are used which require extremely small current at balance.

Potentiometers are used for accurate measurement of emf of electrochemical cells. They operate on the Poggendorff's compensation principle. In this method an unknown emf is opposed by another known emf until the two are equal as shown by no deflection on a galvanometer present in the circuit.

The potentiometer, as shown in fig. consists of a uniform wire AB. A storage battery (K) is connected to the ends A and B of the wire through a rheostat ®. The cell of unknown emf (X) is connected in the circuit by connecting its positive pole to A and the negative pole to A and the negative pole is connected to a slid and contact (D) through a galvanometer (G). The sliding contact (D) is freely moved along the wire AB till no current flows through the galvanometer, Then the distance AD is measured. The emf of unknown cell is directly proportional to the distance AD.D

$$E_x \, \alpha AD$$

Then the unknown cell(X) is replaced by a standard cell (S) in the circuit. The sliding contact is again moved till there is null deflection in the galvanometer. Then the distance AD' is measured.

The emf of standard cell Es is directly proportional to the distance AD'

$$E_s \, \alpha AD'$$

Then, the emf of the unknown cell can be calculated from the following equation,

$$\frac{\text{Emf of the unknown cell (X)}}{\text{Emf of the standard cell (S)}} = \frac{\text{Length AD}}{\text{Length AD'}}$$

$$\frac{E_x}{Es} = \frac{AD}{AD'}$$

Emf of the unknown cell $Ex = \frac{AD}{} \text{ X } Es$