

pH Measurements with a Glass Electrode Withstanding 1500 kg/cm² Hydrostatic Pressure

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A glass electrode can be made to withstand high hydrostatic pressure, up to 1500 kg/cm², by separating the inside fluid from the outside one with a layer of silicone oil acting as a liquid piston, enabling the inside and outside pressure to compensate continuously. Such a glass electrode, with two Ag-AgCl electrodes, maintains its hydrogen electrode function at high pressure. pH changes resulting from dissociation constant shifts caused by pressure in acid and buffer solutions have been measured in good agreement with theoretical expected values for HCl, acetic acid, carbonic acid, and acetate buffer. No agreement was found for bicarbonate buffer. Phosphate buffer and sea water have also been tested. An adapted version of the cell-assembly is planned to equip the French bathyscaphe for deep-sea investigations.

BATHYSCAPHES make it possible to make deep sea investigations with complex man-operated laboratory equipment. pH determinations at great ocean depth are of interest in the field of oceanography, and this work was undertaken with the aim to build a pH meter to be used on the French bathyscaphe.

In this paper, we will describe the properties of a glass electrode assembly submitted to high pressure, and give details about the laboratory test equipment.

GENERAL PRINCIPLE

The chosen electrode assembly consists in a bulb-type Corning 0.15 glass electrode with two silver-silver chloride reference electrodes. The glass electrode is partly filled with 0.1N HCl and the hydrostatic pressure inside and outside are made to compensate continuously, as shown in the simplified drawing of Fig. 1, by interposing a chemically inert, immiscible, high insulating fluid between the inner and outer aqueous solutions. The density and compressibility of this fluid must be such that its density never exceeds that of water at the highest pressure investigated, i.e., 1500 kg/cm². Silicone polymers meet all these requirements, and we have used a silicone fluid MS 200 of viscosity 1 centistoke at 25° made by Midland Silicones Ltd, London.

Figure 2 shows another arrangement better suited for laboratory work. The investigated solution is trapped in a chemically inert container and any contamination from the outer steel pressure chamber is avoided. Pressure is applied to the piston by means of a hydraulic press.

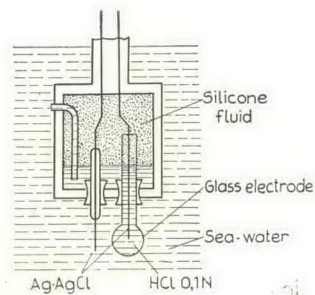


FIG. 1. Schematic drawing representing the glass-electrode assembly for measuring pH at great ocean depth.

CONSTRUCTION OF THE ELECTRODE ASSEMBLY AND PRESSURE CHAMBER

Figure 3 represents a vertical cross section through the glass electrode assembly and the pressure chamber. Electrical connections are made through a Pyrotenax multilead cable (Cablerie de Clichy, France). Two of the twelve copper leads which are imbedded in an insulating mineral powder are shown. The other leads provide additional connections for temperature recordings by means of thermocouples, for detecting static electricity, and for eventual conductivity measurements.

Both ends of the cable are filled with a cold-setting potting resin, Araldite type D (Ciba, Basel, Switzerland). The outer copper shell of the cable is brazed to the steel bomb head carrying the electrode assembly.

The silver-silver chloride electrodes consist of pure silver wire (1.6-mm diam) coated with silver chloride by electrolysis. Great care should be taken to avoid any scratches, and it is recommended to use protecting sleeves on mounting. The upper rim of the glass electrode is for the same reason covered with a soft polythene ring.

The frame which supports the electrodes is made of Perspex plastic, and can easily be taken to pieces for replacement of the electrodes.

The bore through the steel base leads to a manometer and to a smaller upright cylinder (20 mm i.d.) with a piston to which pressure is applied between the plates of a ten-ton laboratory hydraulic press. The piston, terminated with a rubber cup gasket, is in contact with a lubricating

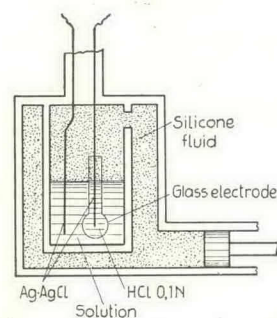


FIG. 2. Schematic drawing representing the glass-electrode assembly for measuring pH at high hydrostatic pressure with a laboratory equipment.

layer of oil which is separated from the silicone fluid, with which it is miscible, through a layer of water. Compression sends water into the main chamber, but the volumes are adjusted to avoid any contamination of the solution outside the electrode.

ELECTROMETER

The electrometer is the same as that described by Distèche and Dubuisson.¹ A d'Arsonval galvanometer is used for zero readings and the emf is measured with a precision slide wire potentiometer, the dial of which reads directly to 0.1 mv. It is calibrated with a Weston standard cell. The over-all sensitivity corresponds to 27-mm scale deflection for 1 mv.

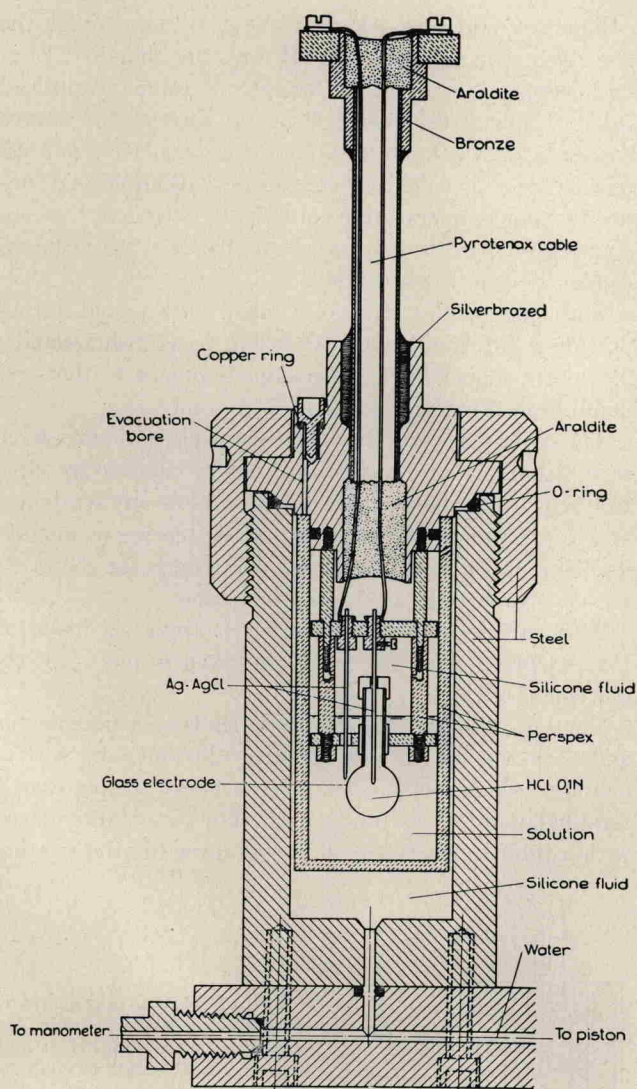


FIG. 3. Cross section through the glass-electrode assembly and pressure chamber.

¹ A. Distèche and M. Dubuisson, *Rev. Sci. Instr.* **25**, 869 (1954).

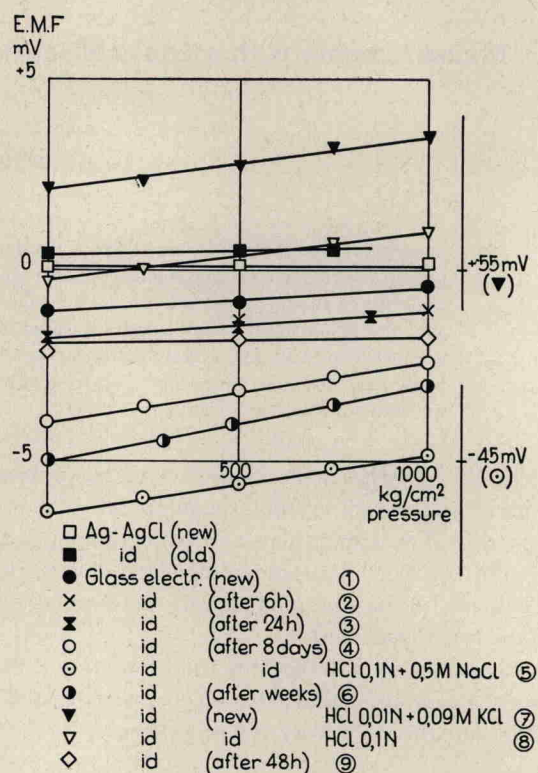


FIG. 4. Variation of the glass-electrode asymmetry potential with pressure. The scales for lines 5 and 7 are on the right.

RESULTS

Glass electrodes of the type described have been tested up to 1500 kg/cm² without damage. They maintain their hydrogen electrode function and there is no hysteresis, i.e., no zero shifts.

For all the electrolytes so far investigated the emf of the cell always varies linearly with increasing pressure as shown in Figs. 4-6.

This is true provided precautions are taken to minimize the temperature effects caused by the more or less adiabatic stepwise compression or decompression of the silicone fluid.

To evaluate these temperature effects at their maximum, sudden pressure steps of 1000 kg/cm² reached in 40 sec have been applied and the temperature changes recorded at various sites inside the electrode vessel with thermocouples (Cu-Constantan cold junction inside the potted lower end of the multilead cable).

The results indicate a quick temperature rise of 3°C in the silicone fluid followed by an exponential decay, the initial temperature being reached again after 10 min. In the water solution, the temperature rise never exceeds 1°C, the maximum being attained after 5 min, and final equilibration requiring 30 min. It appears also that the temperature changes slightly differ from place to place in the electrode vessel.

To minimize these effects which affect the emf of the cell