

Note

A new, modified flow-through polarographic detector

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In a previous paper¹ a completely new type of flow-through polarographic detector was described, based on the introduction of the analyte into a space filled with mercury², and for comparison the previous literature on the characteristics of other polarographic detectors was cited. The detector has a horizontal inlet jet, and the solution introduced forms a thin film between the outer surface of the jet and the mercury forming the surface of the working electrode. In this arrangement the detector exhibits a very rapid response which makes it especially suitable for use in high-performance liquid chromatography (HPLC). The present paper describes a modified detector of this type, and compares its properties with those of the original model, tested under similar conditions.

EXPERIMENTAL

Detector construction

The most important part of a detector of this type is the liquid junction between the reference and working mercury electrodes. In the original construction a porous ceramic jet, covered with a special lacquer on the side facing the mercury, was used (Fig. 1a). The lacquer was removed on the jet tip, thus forming a small uninsulated area providing electrical connection. A drawback of this arrangement is the relatively tedious preparation of the jet, involving machining and boring of the ceramic, insulation with the lacquer and lacquer removal on the jet tip.

In the new construction the liquid junction is provided by a thin layer of the electrolyte between the conical surface area of the inlet jet and the conically shaped wall of the reference electrode space (Fig. 1b). The coaxial conical planes have apex angles of 70 and 80°, respectively, and their apices are provided with openings 0.2 mm in diameter, through which the analyte passes into the space filled with mercury.

The detector assembly, made of organic glass, except for the seals and the inlet capillary, is depicted in Fig. 2. There are four main parts connected by a thread (represented by the dashed line in the figure). In the wall of the reference electrode compartment, a valve analogous to those in bicycle tyres is placed, through which the compartment is filled with the electrolyte for a saturated silver–silver chloride reference electrode. The wall of the mercury electrode compartment is provided with

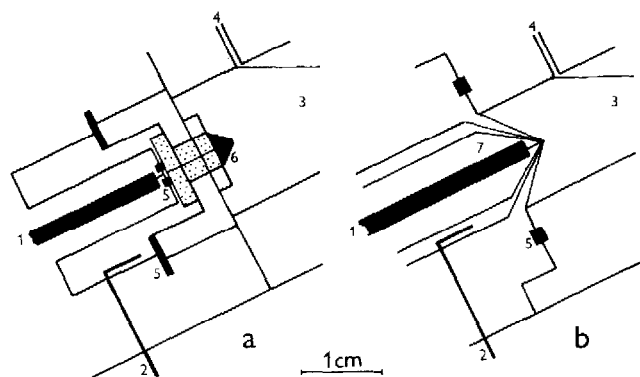


Fig. 1. Liquid junction between the working and the reference electrodes in the original (a) and the modified (b) detector. 1 = Stainless-steel inlet capillary (auxiliary electrode); 2 = contact with the silver-silver chloride reference electrode; 3 = mercury; 4 = channel to waste; 5 = rubber seal; 6 = porous ceramic jet; 7 = inlet jet.

two openings. The upper opening has a screw-in socket fitted with a plastic tubing through which the solution is led to waste after detection (a vessel placed *ca.* 0.5 m under the detector). The other opening, placed in the detector axis, is an auxiliary opening (see preparation of the detector for measurement) and is closed during actual measurement. The electrical contact to the working electrode is provided by a platinum wire passing through the detector wall.

Instruments and chemicals

The detector was tested in a liquid loop consisting of an SP8770 isocratic pump (Spectra-Physics, U.S.A.), and injection valve with a 20- μ l loop 7125 (Rheodyne, U.S.A.) and a glass chromatographic column (150 \times 3.2 mm I.D.) packed with separon SIX C18, 5 μ m (Laboratorní Přístroje, Czechoslovakia). A three-electrode polarograph was assembled from operational amplifiers. The current signal was recorded by a TZ4200 line recorder (Laboratorní Přístroje) or by a storage oscilloscope PM3219 (Philips, The Netherlands).

o-Nitrophenol, detected at a potential of -1.1 V in a 0.1 M acetate buffer of pH 4.6 containing 50% methanol, was chosen as the model substance, as in the testing of the previous model of the detector.

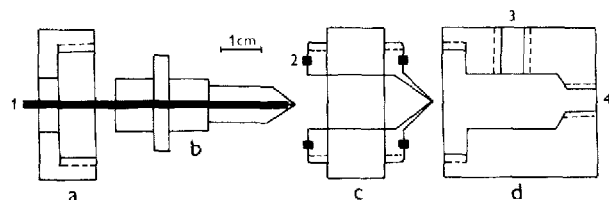


Fig. 2. The detector assembly. a = Cap nut; b = inlet jet; c = reference electrode compartment; d = working electrode compartment; 1 = inlet capillary; 2 = silicone rubber seal; 3 = outlet opening; 4 = auxiliary opening.

RESULTS AND DISCUSSION

Preparation of the detector for measurement

After screwing the individual parts of the detector together, the cap nut is loosened so that the tip of the inlet jet is brought about 1 mm from the wall of the reference electrode compartment. The detector is turned so that the axis of the inlet jet is directed upwards and the space is filled with a saturated solution of potassium chloride using a syringe. The cap nut is tightened and the detector turned to the operating position, *i.e.*, with the inlet jet axis at an angle of about 45°. The working electrode compartment is filled with mercury, the following liquid is introduced into the detector until the tubing to the waste is filled and the auxiliary opening is opened. The siphon effect causes the mercury and the liquid to flow up to the level of the outlet (Fig. 1b). The auxiliary opening is then closed and the working electrode is preconditioned for about 15 min at the working potential. The detector is then ready for measurement.

Detector performance

The response rate, the reproducibility and the linear dynamic range were tested. A 500- μ l volume of the model solution ($2 \cdot 10^{-5}$ M *o*-nitrophenol) was injected directly into the detector. The response rate was affected little by the material and the construction of the electrolyte junction between the working and reference electrodes. For example, the time constants of the response obtained with the original detector model at flow-rates of 0.3, 0.5 and 0.9 ml/min were 1.34, 0.65 and 0.26 sec, respectively; with the modified detector, the corresponding values under the same conditions were 1.1, 0.50 and 0.20 sec. The reproducibility of the response was tested in the chromatographic system by measuring the peak heights after injecting 500 ng *o*-nitrophenol at a flow-rate of 0.5 ml/min. The relative standard deviation of the peak height (1.4%) in a series of 20 injections represents the reproducibility of the whole chromatographic measurement. However, the scatter was substantially larger when samples were injected directly into the detector. One reason for this is the renewal of a thin layer of the analyte between the mercury and the poorly wettable surface of the organic glass immediately after the turning of the injection valve. This effect was not observed with the original detector model, because of the presence of the wetted ceramic surface.

The linear dynamic range of the response was also measured in the chromatographic system, using a known injected amount and measuring the peak volume³. A linear calibration curve with a slope of 6.0 A/g and a correlation coefficient of 0.9987 was obtained from 10 to 1000 ng *o*-nitrophenol. An amount of 10 ng of the substance yields a chromatographic peak whose height equals three times the peak-to-peak amplitude. The limits of this linear range correspond to concentrations of $1.8 \cdot 10^{-7}$ and $1.8 \cdot 10^{-5}$ M at the peak maximum. The upper concentration limit of the linear response practically corresponds to the value ($2 \cdot 10^{-5}$ M) obtained with the original detector model having a horizontal ceramic jet (0.2 mm I.D.).

CONCLUSION

The modified detector exhibits suitable properties for use in HPLC, similar to

the original model. An advantage of the new construction is its simpler manufacture, using a single material, organic glass.

REFERENCES

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- 3 R. P. W. Scott, *Liquid Chromatography Detectors*, Elsevier, Amsterdam, Oxford, New York, 1977, p. 11.