Chimia 43 (1989) 10–11

An Ion-Selective Photodiode (ISPD)**

Philippe M. J. Périsset, Peter C. Hauser, Susie S. S. Tan, Kurt Seiler, Werner E. Morf, and Wilhelm Simon *

Abstract: A simple ion-selective chemical sensor with an optical transduction (optode) based on a photodiode with limited spectral response is described.

Optodes are becoming increasingly popular and a multitude of designs has been reported recently[1–4]. All these devices are based on absorption, fluorescence or reflection and rely on a light source and a detector. Optical fibres are often employed to bring the incident light to the sensing area and guide it back to the detector. Spectral selectivity is achieved conventionally using monochromators or in some cases with light emitting diodes (LEDs) having a relatively narrow spectral output.

Here we report on a compact probe that consists of a photodiode coated with a poly(vinyl chloride) (PVC) membrane containing a chromoionophore. Spectral selectivity is achieved by using a light sensitive device that has a filter built-in and ambient light as light source. The diode is embedded in the end of a plastic barrel and the entire assembly can be dipped into solutions similar to an ion-selective electrode.

The membrane belongs to a new class of optode membranes recently described, that rely on the ion transfer from a sample into a PVC membrane induced by ionophores[5–7]. Formally two basic principles are possible for such devices: An ion exchange facilitated by one or more charged or neutral carriers in the membrane phase or an ion co-extraction from the sample into the membrane phase by employing two neutral carriers for cations and anions respectively. In the former case the response will be controlled by a ratio of ion activities in the sample solution, while in the second case the response is controlled by a product of ion activities in the sample solution to which the employed carriers induce selectivity. It is also possible to employ a combination of the two mechanisms. In either case at least one of the carriers has to contain a chromophore and must therefore be a chromoionophore[5–7].

In the present case, the $K^{\oplus}$ to $H^{\oplus}$ activity ratio ($a_{K^{\oplus}}/a_{H^{\oplus}}$) was measured by using a membrane containing 4-bis(2-butyryloxyethyl)amino-4′-trifluoroacetylazobenzene (chromoionophore ETH 6004)[8], a carbonate-selective carrier that responds also to protons, and tetraphenylborate (potassium salt) as exchange sites for cations. The chromoionophore ETH 6004 shows an absorption band at $\lambda = 455$ nm in the unprotonated form which changes to about 560 nm when protonated. The photodiode has optimal response in the range from about 650 nm to 400 nm with its peak response at 560 nm, so that the presence of the protonated form of the chromophore can be adequately monitored.

In Fig. 1 the response of this optode to the potassium to hydrogen ion activity ratio is compared to measurements obtained using a conventional spectrophotometer. It is obvious, that the responses are quite comparable. They are in agreement with the theoretical description[5–7]. Here the transmittance rather than the absorbance values are plotted, since it is the former parameter that relates directly to the light intensity measured by a photodiode. The response of the ion-sensitive photodiode described here is of course dependent on the ambient light and care has to be taken to ensure that fluctuations of the incident light intensity during a measurement/calibration cycle are minimized. Sufficiently stable light conditions can easily be achieved by placing a desk lamp near the detector, but it has to be assured that the geometrical arrangement of ISPD, lamp, and sample containers are kept constant from one measurement to the other. Another possibility to eliminate the influence of fluctuations in ambient light intensity, would be to place a second photodiode that does not carry an ion-sensitive membrane close to the detector diode, and to perform measurements in a differential mode.

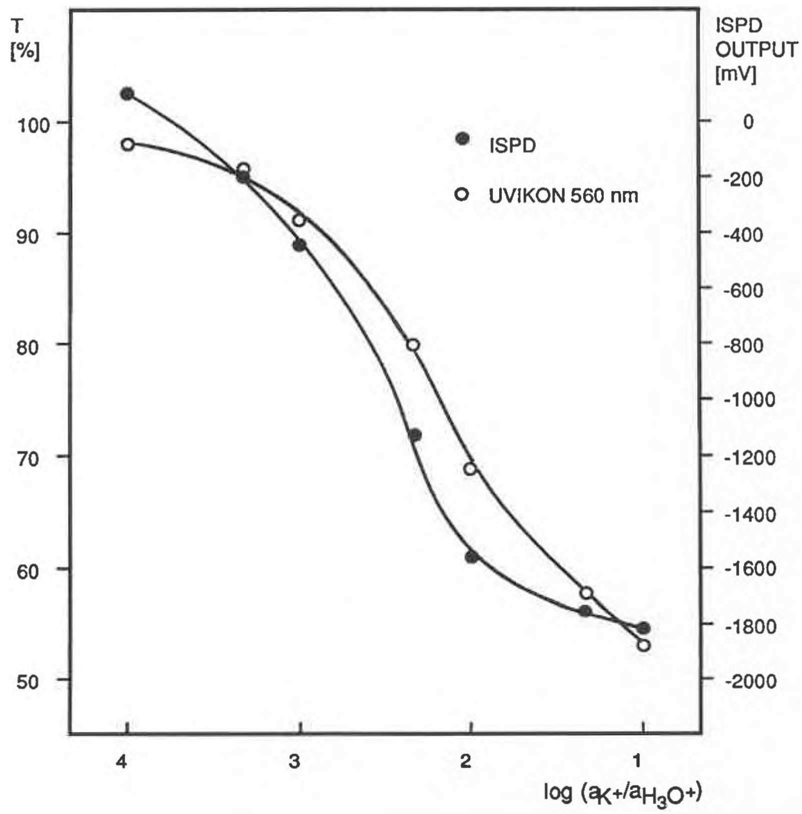

Fig. 1. Calibration curves obtained with the ISPD and a conventional spectrophotometer.

* *Correspondence:* Prof. Dr. W. Simon
Laboratorium für Organische Chemie
Eidgenössische Technische Hochschule Zürich
ETH-Zentrum, Universitätstrasse 16
CH-8092 Zürich

** *Acknowledgement:* This work was partly supported by the Swiss National Science Foundation (grant No. 2000-4.917 and 2000-5.485).

Experimental:

The ion-sensitive membrane consisted of 4 mg ETH 6004, 7 mg potassium tetraphenylborate (Fluka), 84.8 mg poly(vinyl chloride) (PVC high molecular, Fluka), and 155 mg bis(2-ethylhexyl)sebacate. The mixture was dissolved in 1.5 mL tetrahydrofuran (THF, Fluka) that was distilled to remove the stabilizer and applied to the diode with a micropipette.

The photodiode was from Sharp Corporation (Model No.: BS-500B; supplier: Omni Ray AG, Zürich). This device has a flat active area of 2 × 3 mm and was glued (Cyanolit®, 3M AG, Rüschlikon) into the end of a plastic tube of 10 mm diameter and 12 cm length. The photocurrent was measured by reverse biassing the diode with a constant − 5 V to the virtual ground input of an operation amplifier (Texas Instruments TL 074CN) in the current follower configuration and reading the voltage with a conventional digital voltmeter. The input of the operational amplifier was also equipped with an adjustable current source to provide an offset facility. The conventional spectrophotometer was a UVIKON Model 810 (Kontron AG, Zürich) and the corresponding membrane (thickness ≈ 1 μm) was cast on a 35 mm diameter glass plate (Herasil quartz glass, W. Möller AG, Zürich) mounted in a homemade flow-through cell. The solutions were made up from analytical reagent grade KCl and HCl.

Received: January 23, 1989 [FC 157]

[1] W. R. Seitz, *Anal. Chem.* *56* (1984) 16 A.
[2] O. S. Wolfbeis, *Fresenius Z. Anal. Chem.* *325* (1986) 387.
[3] N. Opitz, D. W. Lübbers, *Int. Anesthesiol. Clin.* *25/3* (1987) 177.
[4] J. Janata, A. Bezegh, *Anal. Chem.* *60* (1988) 62 R.
[5] W. E. Morf, K. Seiler, B. Lehmann, C. Behringer, K. Hartman, W. Simon, *Pure Appl. Chem.*, in press.
[6] W. E. Morf, K. Seiler, B. Lehmann, C. Behringer, S. Tan, K. Hartman, P. Sörensen, W. Simon, paper presented at the 5th Symposium for Ion-Selective Electrodes in Matrafüred, Hungary (1988).
[7] W. E. Morf, K. Seiler, P. Sörensen, W. Simon, paper presented at the 5th Symposium for Ion-Selective Electrodes in Matrafüred, Hungary (1988).
[8] C. Behringer, B. Lehmann, W. Simon, *Chimia* *41* (1987) 397.

Chimia 43 (1989) 11–12