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Note

Solid-state coulometric cell as detector for gas chromatography

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In recent years solid-state chemical sensors of various working principles have become important in the analysis of inorganic compounds and hydrocarbons. Thus, homogenous semiconductor sensors for the quantitative analysis of oxidable or reducible compounds have been described. Semiconductive thin-film detectors have been combined with gas chromatography (GC)[1–3], but in comparison with other GC detectors their sensitivities were too low. More favourable is the use of solid-state coulometric cells with GC columns. This paper presents some results from investigations with solid-state coulometric cells.

The idea of the method is to use coulometrically generated oxygen in a feedback fashion, thereby generating a detector response according to oxygen demand. The overall principle is the same as in the servomechanism detector by Littlewood and Wiseman[4], applied in a different manner.

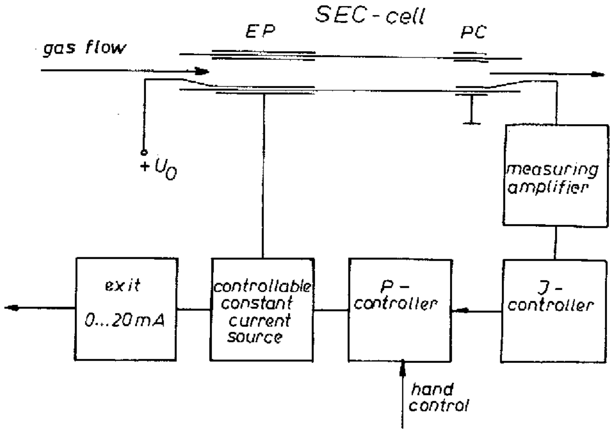

Fig. 1. Scheme of the solid-state coulometric cell.

BASIC CONCEPT OF THE SOLID-STATE COULOMETRIC CELL

The solid electrolyte cell applied as a GC detector is a four-electrode arrangement with porous platinum layers on a zirconia–calcia solid electrolyte tube, shown schematically in Fig. 1[5–7]. The carrier gas flows through the tube, which is surrounded by air as a reference gas. The first electrode system (EP-electrolytic pump) is used for oxygen dosage according to Faraday's law, and the second (PC-potentiometric cell) serves for the open-circuit measurement of Nernst voltage. The two electrode systems are heated separately in electrical furnaces. In connection with the electrical circuit, the cell can be used for coulometric titration of small amounts of oxidable components in the inert gas flowing through the cell. The open-circuit voltage is measured by a high ohmic amplifier. From the amplified voltage the guide is derived for the dosing current controller.

The main characteristics of the cell are as follows. Solid electrolyte tube: zirconia, stabilized by calcium oxide (300 mm × 6 mm O.D. × 3 mm I.D.); coulometric part of the cell: length of electrodes, 80 mm; temperature, 650–750°C; potentiometric part of the cell: length of electrodes, 5 mm; temperature, 700°C; nominal gas flow-rate, 3–6 l/h; dosing currents, 0–20 mA.

The dosing current I controlled the oxygen flow q_{O_2} passing the solid electrolyte well:

$$\frac{\mathrm{d}q_{O_2}}{\mathrm{d}T} = \frac{I \cdot V_o}{4\,F}$$

where V_o is the molar volume and F is Faraday's number.

For the coulometric titration of oxidizable components in a carrier gas it is suitable to adjust the control-point setting some ppm of oxygen above the equivalence, *i.e.* in the region of 200–220 mV. Then the concentration of any oxidizable component X is given by

$$c_X\,(\mathrm{ppm}) = \frac{1}{Z}\left[\frac{209 \cdot I}{v_g} - 10^6 \cdot P \cdot \exp\left(-\frac{4FU}{RT}\right)\right]$$

where Z = number of oxygen equivalents per molecule of X; I = dosing current in mA; v_g = carrier gas flow-rate in l/h; P = gas pressure; R = gas constant; U = open-circuit voltage; T = temperature of the potentiometric cell (973 K).

The amount of oxidizable component dosed in the carrier gas is given by

$$G_X = \frac{1}{Z}\frac{M_X}{2F}\int_{t_1}^{t_2} 10^6\,[I\,(t) - I_o]\,\mathrm{d}t$$

where M_X = molecular weigth of X; I = titration current in the presence of the sample; I_o = titration current in the absence of the sample; t = time.

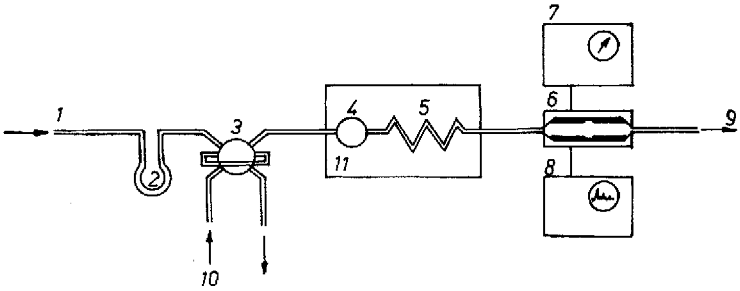

Fig. 2. Scheme of the experimental arrangement: 1 = carrier gas stream (argon R 50); 2 = pre-column molecular sieve 5A; 3 = sampling valve; 4 = injection port; 5 = GC column (1 m × 4 mm I.D., stainless steel, filled with molecular sieve 5A or Porapak QS); 6 = coulometric cell; 7 = power supply; 8 = recorder; 9 = carrier gas outlet; 10 = sample gas stream; 11 = thermostat.

EXPERIMENTAL

The experimental arrangement consists of a conventional GC device equipped with the ceramic unit described above as detector (Fig. 2). The carrier gas (1) is purified by a molecular sieve column (2), the sample gas is added through the sampling valve (3) or by a gas-tight syringe by the injection port (4), the carrier–sample mixture passes through the GC column (5) and the separated substances enter the detection unit (6), originating a signal, proportional to the sample concentration, which is registrated by the recorder (8). The GC column is connected to the ceramic cell by a stainless-steel capillary of 30 cm length and a dead volume of *ca.* 1 µl, negligible compared with the volume of the ceramic cell (2 cm^3).

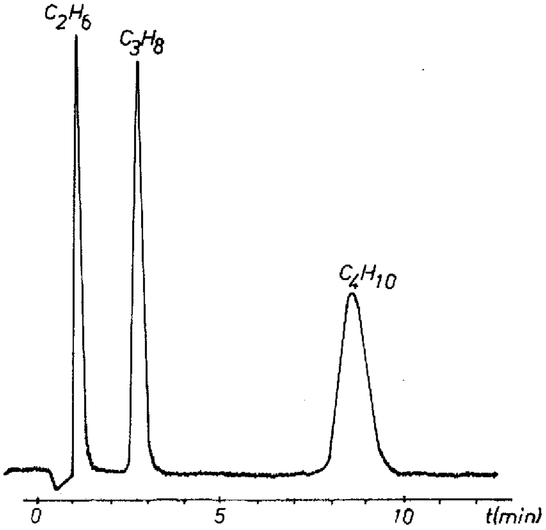

Fig. 3. Determination of hydrocarbons with the solid-state coulometric cell. Column, 2 m × 4 mm I.D., Porapak PS; carrier gas, argon R 50; temperature, 100°C; sample size, $1.1 \cdot 10^{-7}$ g of ethane, $1.6 \cdot 10^{-7}$ g of propane, and $2.2 \cdot 10^{-7}$ g of butane.

TABLE I

SENSITIVITY AND DETECTION LIMIT OF THE CERAMIC CELL FOR SEVEN SUBSTANCES

Compound	*Sensitivity* *($mV/mg\ cm^{-3}$)*	*Detection limit*	
		$mg\ cm^{-3}$	*ppm*
Oxygen	$1.7 \cdot 10^5$	$5.8 \cdot 10^{-8}$	0.3
Hydrogen	$5.3 \cdot 10^3$	$1.9 \cdot 10^{-6}$	160
Nitrous oxide	$4.45 \cdot 10^2$	$2.25 \cdot 10^{-5}$	85
Methane	$7.4 \cdot 10^4$	$1.35 \cdot 10^{-7}$	1.4
Ethane	$8.5 \cdot 10^4$	$1.2 \cdot 10^{-7}$	0.7
Propane	$1.1 \cdot 10^6$	$9.25 \cdot 10^{-8}$	0.35
Butane	$8.5 \cdot 10^4$	$1.2 \cdot 10^{-7}$	0.35

RESULTS

The arrangement described is suitable for the determination of traces of inorganic compounds and hydrocarbons. The response of the ceramic cell was studied with oxygen, hydrogen, nitrous oxide, methane, ethane, propane and butane. Fig. 3 shows a chromatogram of $1.1 \cdot 10^{-7}$ g of ethane, $1.6 \cdot 10^{-7}$ g of propane and $2.2 \cdot 10^{-7}$ g of butane. The sensitivity and the detection limits of the cell related to the test substances are listed in Table I. Because the solid-state coulometric cell is a concentration-dependent detector, the sensitivity is given in terms of $mV/mg\ cm^3$ and consequently the detection limit is in terms of mg/cm^3. The data in column 4 (detection limit in ppm) are related to a sample volume of 1 cm^3. The extension of the linear dynamic range of the detector is greater than 10^3.

The first investigations show that the ceramic cell working as GC detector in combination with a GC arrangement makes possible the detection of oxygen and hydrocarbons down to the ppb region*. Further investigations with an optimized arrangement (reduced cell volume, improved adaptation of the cell to the gas chromatograph) will provice more detailed information about the suitability of the coulometric cell as a GC detector.

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* The American billion (10^9) is meant.