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NEW TYPE OF ELECTROCHEMICAL SULPHUR-SENSITIVE DETECTOR FOR GAS CHROMATOGRAPHY

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SUMMARY

A new type of electrochemical, sulphur-sensitive detector for gas chromatography has been constructed. Its operation is based on the reduction of iodine by sulphur dioxide, but the unique design of the detection cell assures a much longer lifetime of the electrolyte solution and a more rapid response compared with the majority of coulometric detectors. This is achieved by application of a large total volume of the electrolyte solution (*ca.* 320 cm³) and -simultaneously- a small working volume of the cell proper (*cu.* 2.8 cm³). In combination with a mineralization furnace, it yields very close values of the degree of conversion of organic sulphur into SO₂ for different classes of sulphur compounds ($\pm 4\%$ relative). Disconnection of the oxygen supply to the furnace reduces the number of the compounds being detected to those which are able to react with iodine directly, e.g., SO₂, H₂S, mercaptans. The S/C selectivity ratio is higher than 10⁶. The sensitivity of the detector depends not only on the amplification, but also on the iodine concentration selected. The detector signal is generally non-linear; however, for any iodine level, the linear range is about two orders of magnitude. Absolute detection limits are 5.4 and 19 pg S per second for the minimum and most often applied iodine levels, respectively.

INTRODUCTION

The determination of sulphur compounds, especially in environmental pollutants, requires the development of new sulphur-sensitive detectors for gas chromatography (GC). In this context, electrochemical detectors have played a significant role. Microcoulometric detectors constructed according to Coulson and Cavanagh^{1,2} are based on a follow-up system which maintains constant the concentration of an active component of the electrolyte solution. Such detectors and their applications have been reviewed by Killer³. Two types of these continuous titrators are commercially available: Microcoulometric Titration System from Dohrmann, Envirotech Corp. (Santa Clara, CA, U.S.A.) and Antek Model 710/771 from Antek Instruments (Houston, TX, U.S.A.). Although applied in numerous studies, they suffer from some disadvantages as GC detectors and are utilized mainly in elemental microanalysis for sulphur, chlorine, nitrogen and phosphorus. The main disadvantages are poor dy-

dynamic properties resulting in up to 30% broadening of "fast peaks", $t_R \leq 1$ min, due to relatively large operating volumes (5520 cm^3), and the short lifetime of the electrolyte solution owing to the small (with regard to this feature) operating volumes. Their main advantage is a very wide linear range. Systems of this kind are used as continuous monitors of SO_2 in air (large volumes up to 1 dm^3 and time constants of up to a few minutes).

A different microcoulometric GC detector is that of Ševčík⁴ and Krichmar and co-workers⁵⁻⁷. Other electrochemical principles utilized in GC detectors are potentiometry⁸⁻¹¹, amperometry¹² and conductometry¹³⁻¹⁷. Comparisons of the different types of electrochemical detectors, and also with other selective GC detectors, have been presented in reviews^{3,18,19}.

A third generation Hall electrolytic conductivity detector, initially introduced mainly as a nitrogen-sensitive detector¹⁴, has recently been evaluated in a sulphur-selective mode with excellent results²⁰. The instrument is produced by Tracor (Austin, TX, U.S.A.) as Model 700 A and has a detection limit of $0.85 \text{ pg S per second}$ for diethyl disulphide, which is a factor of > 20 lower than that of the Tracor flame photometric detector under identical conditions. An additional virtue of the Hall detector is its more linear response.

The common feature of most of the above mentioned detectors is the utilization of a mineralization furnace. For sulphur, both oxidative and reductive modes can be applied; however, the first mode suffers from incomplete conversion of organic sulphur, S_{org} into SO_2 , and the second from the inconvenience of utilization of hydrogen. Usually, the degree of conversion does not depend exclusively on the furnace construction and operating conditions but also on the kind of sulphur compound and sample matrix. Incomplete conversion leads to the necessity of calibration even for microcoulometric detectors³, sometimes also for individual compounds*⁹. A paper by White²¹ in which an oxidative furnace was said to be compound and matrix independent has not been developed further in the literature. Significant improvements in this field were achieved by utilization of WO_3 as a catalyst²²⁻²⁴.

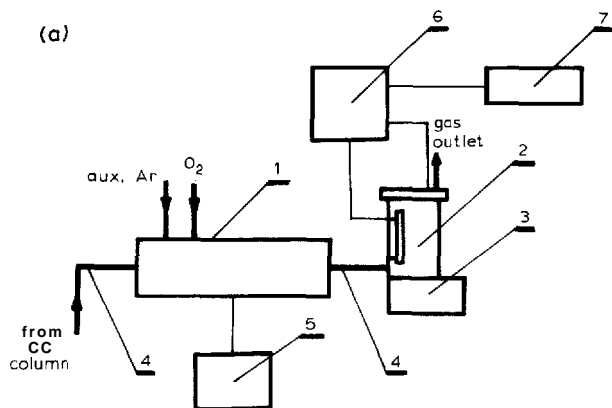


Fig. I.

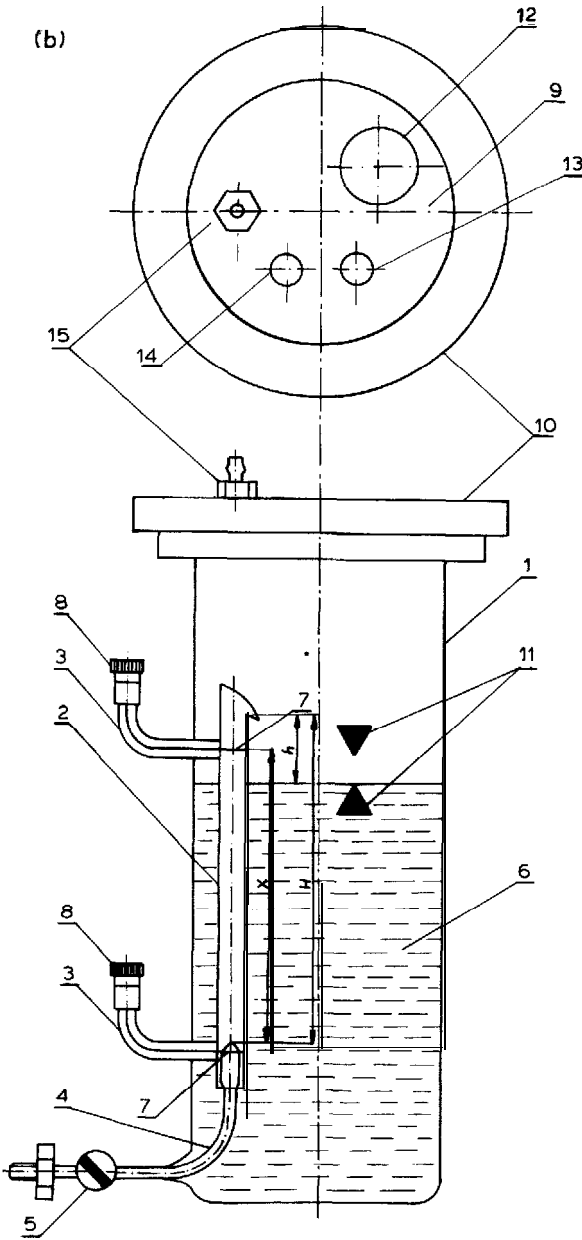


Fig. 1. Schematic diagram of the detection system (a) and cross-section of the cell (b). a, 1 = Mineralization furnace; 2 = detection cell; 3 = magnetic stirrer; 4 = heated gas connections; 5 = furnace temperature-control unit; 6 = cell operation control unit; 7 = recorder. b, 1 = Main cylinder; 2 = detection tube; 3 = supports; 4 = inlet tube with injection capillary; 5 = three-way stop-cock; 6 = electrolyte solution; 7 = detection electrodes; 8 = screw terminals; 9 = plexiglass cover; 10 = set screw; 11 = level marks; 12 = cathode position; 13 = SCE position; 14 = anode position; 15 = gas outlet pipe.

EXPERIMENTAL

Detector design

The detection system is shown in Fig. 1a. It consists of a furnace (1), detection cell (2), magnetic stirrer (3), heated gas connections (4) and two electronic modules, the furnace temperature-control unit (5) and the cell operation control unit (6). Units 1-4 are mounted on the **exchangable** head of the oven of a Model 504 gas chromatograph (MERA-ELWRO, Wroclaw, Poland). The furnace is a quartz tube (45 cm \times 2 mm I.D.) filled with quartz wool impregnated with **WO₃** [introduced as an aqueous solution of ammonium tungstate and decomposed in a stream of oxygen at 950°C; the course of reaction has been independently determined by means of thermal gravimetric analysis (TGA), differential thermal gravimetry (DTG) and differential thermal analysis (DTA)]. The temperature of the main zone of the furnace can be controlled in the range from ambient to 1000°C (\pm 5°C). Additional gas inlets, supplied from the chromatograph-flame ionization detector flow regulators, enable one to maintain a constant flow-rate in the cell and to vary the amount of oxygen employed in the combustion process. Gas connections are made of stainless-steel capillary (1.2 mm I.D.), insulated and heated to 150°C. The total volume of the system between the GC column outlet and the cell inlet is cu. 1.9 cm³.

A vertical cross-section and view of the top of the cell are presented in Fig. 1b. The glass body of the cell consists of a main cylinder (1) with detection tube (2) positioned vertically by means of supports (3) in the former at a distance of ca. 1 cm from the wall of the cylinder. Inlet tube (4) ending in a capillary enters the cell near the bottom of the cylinder. Capillaries are standardized to give a pressure drop of 333 hPa (250 mmHg) at an argon flow-rate of 120 cm³/min. By use of a gas-tight three-way stop-cock (5) the gas stream can be passed directly to the atmosphere, simultaneously preventing back-flow of the electrolyte solution (6). The total volume of the solution in the cell can be varied from 310 to 340 cm³ between the lower and upper level marks (1 1), respectively. Two detection electrodes (7), made of smooth platinum wire (diameter 0.2 mm) in a form of horizontal rings, are sealed into the detection tube and the supports, where they are silver soldered to screw terminals (8). The edge of the main cylinder forms a flange which permits tight sealing of the cell with a plexiglass cover (9) via a silicone rubber gasket and an appropriate set screw (10). Through holes in the cover are positioned the electrodes: platinum cathode (12), SCE reference (13) and platinum anode (14), the first in a separate compartment ending in a Lugin capillary. The gas outlet (15) allows one to measure the gas flow-rate. The electrodes used were Radelkis Types OH-935, OH-937 and OH-932 as cathode, anode and reference, respectively. H, h and X indicate the pumping height, lifting height and absorption height, respectively. The cell construction has been **patented**²⁵.

Injection of a gas stream through the inlet capillary to the detection tube results in an air-lift pump effect and the generated gas-liquid (electrolyte solution) mixture is transported upwards in the tube. The concentration of iodine in the solution is maintained constant at a pre-fixed level. When there are no iodine-consuming species in the gas the e.m.f. measured between the detection electrodes is zero; if the iodine concentration at the upper detection electrode is diminished compared with that at the lower detection electrode the resulting signal can be utilized either for open-loop control of the iodine regeneration current or directly as the output signal of the cell.

Apparatus

The gas chromatograph was equipped with a six-port injection valve and 1.00-cm³ sampling capillary. Chromatographic conditions were as follows: column, 1.9 m × 4 mm I.D., glass; packing, Porapak Q (80–100 mesh) (Hewlett-Packard, Avondale, PA, U.S.A.); column temperature, 130°C; injector temperature, 150°C; carrier gas, argon at 50 cm³/min. Standard mixtures of SO₂ in argon were obtained from a permeation device. A Model K-SO₂ calibrator (PEPW, Chorzów, Poland) was employed with a source efficiency of 223.9 ng SO₂ per min at 36°C, verified periodically by weighing. Approximate measurements of gas flow-rate were carried out with a constriction flow meter and accurate measurements with a movable soap-film flow meter. A Radelkis Type OH-404 coulometer and MERA-ELWRO Model N-5122 pH-meter were utilized in auxiliary experiments. Amplifier modules of Type WO-01 (KABID, Poland) were employed for testing successive versions of the electronic circuit. All numerical calculations were performed by means of HP-25 and TI-59 programmable calculators.

Materials

Potassium iodide, glacial acetic, propionic and butyric acids (POCh, Poland) were of analytical reagent grade. A standard mixture of SO₂, 30 ppm by volume (± 5%) in nitrogen (Norsk-Hydro, Oslo, Norway), was employed as an additional test of the permeation device. All gases used were purified and dried by means of on-line molecular sieve/active carbon filters.

RESULTS AND DISCUSSION

Theory of operation

Considering a differentially small volume, dV_m , of gas-liquid (electrolyte solution) mixture in the detection tube

$$dV_m = dV_g + dV_e \quad (1)$$

where dV_g and dV_e are the differential volumes of gas and electrolyte, respectively, and assuming the absorption of SO₂ is complete on passing the height X (Fig. 1b)

$$c_{\text{SO}_2} dV_g = \Delta c_{\text{I}_2} dV_e \quad (2)$$

where c_{SO_2} is the concentration of SO₂ in the gaseous phase and Δc_{I_2} is the depletion of iodine concentration in the electrolyte solution (both in mol/dm³). Noting that

$$\frac{dV_g}{dV_e} = \frac{v_g}{v_e} \quad (3)$$

where v_g and v_e are volume flow-rates of gas and electrolyte, respectively, we can write

$$A c_{\text{SO}_2} = c_{\text{SO}_2} \cdot \frac{v_g}{v_e} = \frac{w_{\text{SO}_2}}{v_e} \quad (4)$$

where w_{SO_2} is the molar mass flow-rate of SO_2 entering the detector.

The potentials of the upper and lower detection electrodes, E_{UDE} and E_{LDE} , respectively, are

$$E_{\text{UDE}} = E_{\text{I}_2/\text{I}^-}^{\circ'} + \frac{RT}{2F} \cdot \ln \frac{c_{\text{I}_2}'}{c_{\text{I}^-}'} \quad (5)$$

$$E_{\text{LDE}} = E_{\text{I}_2/\text{I}^-}^{\circ'} + \frac{RT}{2F} \cdot \ln \frac{c_{\text{I}_2}}{c_{\text{I}^-}} \quad (6)$$

where $E_{\text{I}_2/\text{I}^-}^{\circ'}$ is the standard (formal) potential of the $\text{I}_2/2\text{I}^-$ redox system, c_{I^-} is iodide concentration (mol/dm^3) in the electrolyte solution, c_{I_2} and c_{I_2}' are the iodine concentrations (mol/dm^3) at the lower and upper detection electrodes, respectively. Thus, the detector signal, ΔE , expressed as the e.m.f. between the two electrodes, is

$$\Delta E = E_{\text{UDE}} - E_{\text{LDE}} = \frac{RT}{2F} \cdot \ln \left(1 - \frac{\Delta c_{\text{I}_2}}{c_{\text{I}_2}} \right) \quad (7)$$

assuming that c_{I^-} is constant. Noting that

$$\Delta c_{\text{I}_2} = c_{\text{I}_2} - c_{\text{I}_2}' \quad (8)$$

and introducing eqn. 4, the final expression for the instantaneous signal, $\Delta E(\tau)$, can be obtained:

$$\Delta E(\tau) = \frac{RT}{2F} \cdot \ln \left[1 - \frac{w_{\text{SO}_2}(\tau)}{v_e c_{\text{I}_2}} \right] \quad (9)$$

Rearranging the above equation and integrating over the time of peak duration, T_0 , gives

$$m_{\text{SO}_2} = \int_0^{T_0} w'_{\text{SO}_2}(\tau) d\tau = M_{\text{SO}_2} v_e c_{\text{I}_2} \int_0^{T_0} \{1 - \exp[K\Delta E(\tau)]\} d\tau \quad (10)$$

where $K = 2F/RT = 0.0778 \text{ mV}^{-1}$ at $T = 298^\circ\text{K}$, M_{SO_2} is the molar mass of SO_2 and $w'_{\text{SO}_2} = w_{\text{SO}_2}/M_{\text{SO}_2}$ is the mass flow-rate of SO_2 .

According to the above the detector should be of the mass-sensitive type (and destructive) with generally non-linear response and sensitivity, defined as

$$S = \frac{d\Delta E(\tau)}{dw'_{\text{SO}_2}(\tau)} = \frac{dA}{dm_{\text{SO}_2}} \quad (11)$$

where A is the peak area, depending on v_e , c_{I_2} and temperature.

Preliminary experiments

The aim of these experiments was to establish the details of cell construction and operation enabling knowledge of the required v_e and c_{I_2} . For the former parameter, studies were made of the influence of cell geometry and electrolyte composition on pumping efficiency and noise level, as well as the validity of the assumption implied in eqn. 2. The main conclusions, which permitted construction of the final version of the cell, are as follows:

(1) the function $v_e = f(v_g)$ is linear for $v_g \geq 150 \text{ cm}^3/\text{min}$ and the latter value was selected for routine operation of the detector

(2) the ratio v_e/v_g depends on h/H but not on v_g when the former is less than a certain critical value (ca. 0.3)

(3) the product of the fraction of the detection tube filled with the electrolyte solution and the volume of the tube comprising the absorption height is the working volume of the electrolyte and in the final geometry of the cell this varies from 1.0 to 1.4 cm^3 for the maximum and minimum h values, respectively

(4) the injection capillaries of the inlet tubes must be standardized

(5) an absorption height, X , of 7.5 cm is satisfactory to achieve complete absorption for the assumed values of v_g and h . This was established by comparing signals for different X values under the same flow conditions and confirmed during the calibration procedure, as discussed later

(6) the time at which the absorption height is passed by the gas-liquid mixture varies from 0.6 to 0.8 sec for the minimum and maximum h values, respectively

(7) gas dispersion is markedly better and baseline noise smaller when the electrolyte solution contains soft surfactants such as carboxylic acids even at small concentrations. Acetic, propionic and butyric acids were examined and the first was chosen at a concentration of 0.4 g/dm^3

(8) the noise level, N , does not exceed 0.02 mV on the average and is independent of the pumping and stirring conditions, but can be influenced by external factors, mainly of the electrical supply network, although screening of the cell is unnecessary.

It was decided to control c_{I_2} , independently of the output signal of the cell, in a closed-loop circuit consisting of the bias voltage source, comparator and current electrodes. The potential of the lower detection electrode (eqn. 6), measured vs. the SCE, serves as a measure of c_{I_2} . Thus, it was necessary to determine the relationship between the potential of the smooth platinum electrode and the iodine concentration in the electrolyte for $c_{I^-} = 0.010 \text{ mol/dm}^3$ and $c_{\text{AcOH}} = 0.4 \text{ g/dm}^3$ (AcOH = acetic acid). This was established by linearization of the potentiometric titration curves. The iodine was generated coulometrically, thus assuring a constant volume of the solution titrated and the samples of SO_2 were so small that the decrease in c_{I^-} never exceeded 1% of the initial value. A typical titration curve is shown in Fig. 2a and its linearized I_2/I^- branch in Fig. 2b. The increases in c_{I_2} , calculated from the number of millicoulombs and the corresponding changes in E yielded the value of the formal potential, $E_{I_2/I^-}^{0'}$. This calculated value was confirmed by continuation of iodine generation until $c_{I_2} = c_{I^-}$, when the measured E is equal to $E^{0'}$ by definition. The average $E_{I_2/I^-}^{0'}$ value was $357 \pm 0.8 \text{ mV vs. SCE}$ (the error was the confidence interval, $t\bar{s}$, for $n = 7$ and $P = 95\%$) corresponding to $+ 597 \text{ mV vs. standard hydrogen electrode}$. Comparison with the literature yielded values of $E^0 = + 536, + 535.5$ and $+ 620 \text{ mV}$ depending on the method²⁶, which are standard potentials, and $E^{0'}$ =

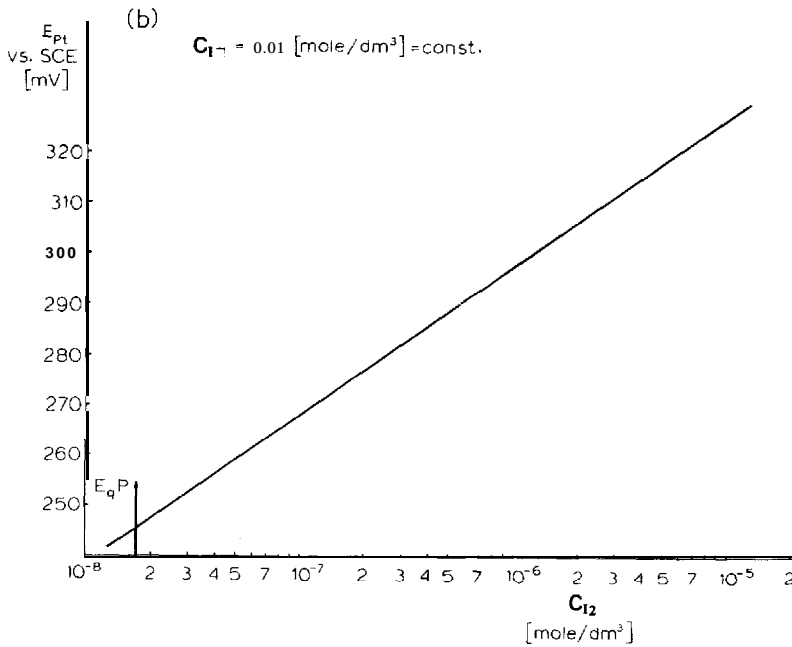
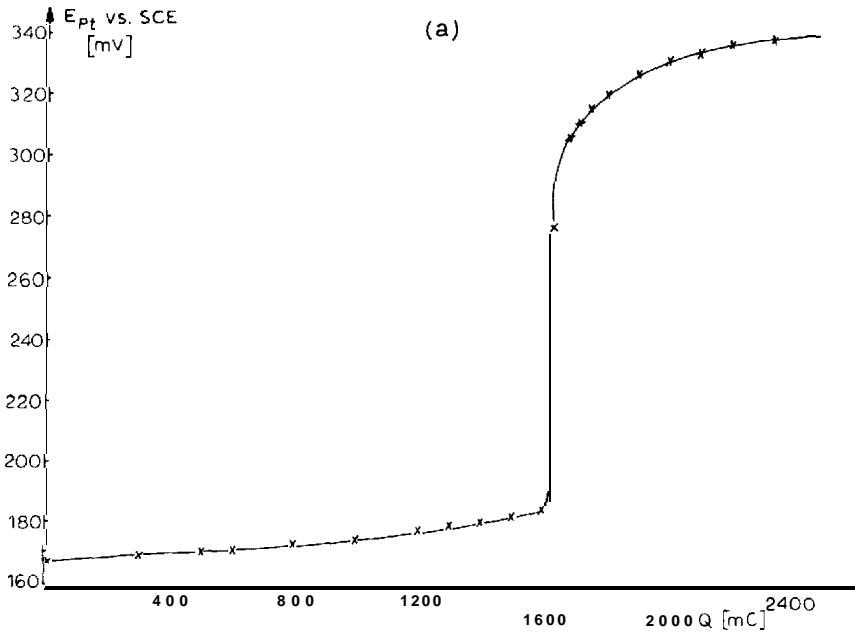


Fig. 2. Potentiometric titration curve (a) of sulphur dioxide by anodically generated iodine. Electrolyte: 0.01 mol/dm³ KI; 0.4 g/dm³ acetic acid. Its I₂/I⁻ branch after linearization is also shown (b).

+ 545 mV the formal potential in 0.5 mol/dm³ sulphuric acid solution²⁷. The difference is probably due to the surfactant properties of acetic acid. Over thirty determinations were made with different platinum electrodes and SCEs and the scatter of the results was ± 2 mV. The potential of the equivalence point, Eq. P, was evaluated less accurately on the basis of the first derivative of the titration curve and it was found that its value ranged from + 337 to + 356 mV.

Calibration curves

Although the detector response was expected to be non-linear, if E_{LDE} represents a fixed point on the titration curve and E_{UDE} a movable one, for sufficiently small ΔE values for which the corresponding part of the titration curve can be approximated by a straight line the calibration curve can be expected to be linear. This was shown experimentally and the calibration curves are presented in Fig. 3, where ΔE_{\max} represents the peak height and m_s is the mass of sulphur injected onto the column. The latter value was set by passing argon at different flow-rates through the permeation source of SO₂. It was found that the Porapak Q column totally retained samples of SO₂ smaller than several micrograms even after 6.h preconditioning at 200°C. Replacement of the column by an identical empty tube gave excellent results; under the same flow and temperature conditions, the apparent "retention time" was

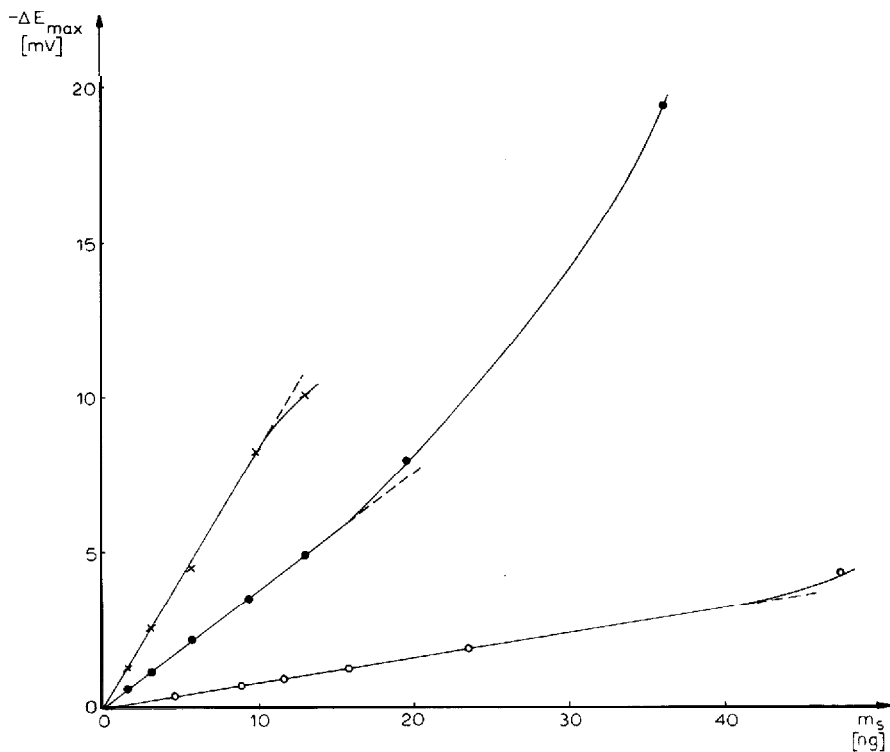


Fig. 3. Calibration curves of the detector obtained by injection of standard mixtures of SO₂ in argon at $T = 298^\circ\text{K}$ and three different iodine concentrations: 0, $5.7 \cdot 10^{-7}$; ●, $1.2 \cdot 10^{-7}$; ×, $2.65 \cdot 10^{-8}$ mol/dm³.

TABLE I
BASIC CHARACTERISTICS OF THE DETECTION CELL CALIBRATED WITH GASEOUS MIXTURES OF SO₂

<i>mV</i>	Iodine concentration level		Sensitivity		Detection limit		Absolute detection limit** (pg S/sec)	Confidence interval, its, for P = 95%, of sensitivity and detection limits (relative)	Linear range (decades)
	<i>mol/dm³</i>	<i>Mass (mV sec/ng S)</i>	<i>Concentration* (mV·m³/mg SO₂)</i>	<i>Mass (ng S)</i>	<i>Concentration* (mg SO₂/m³)</i>				
290	5.7	10 ⁻⁷	0.41	0.52	0.493	0.077	97	0.054 for <i>n</i> = 9	1.9
270	1.20	10 ⁻⁷	2.07	2.59	0.107	0.015	19	0.021 for <i>n</i> = 20	2.2
251***	2.65	10 ⁻⁷	7.37	9.21	0.0489	0.0043	5.4	0.058 for <i>n</i> = 4	2.4

• For a gas flow-rate in the detector of 150 cm³/min.

** For a peak with *b*_{1/2} = 1 sec; the *b*_{1/2} values were different at different iodine levels.

*** In the region of the Eq. P. of the titration curve.

ca. 115 sec due to the large dead volume. Each point on the calibration curve represents an average from five to seven consecutive injections. The precision of the AE values, expressed in terms of the relative standard deviation, S_r , varied from 0.005 to 0.045 and was probably due to the variations in gas flow through the source, especially at very low flow-rates (usually the larger samples resulted in higher S_r values).

As the detector sensitivity depends on c_{I_2} , the curves were determined for three different iodine concentrations: 290, 270 and 251 mV, corresponding to $5.7 \cdot 10^{-7}$, $1.2 \cdot 10^{-7}$ and $2.65 \cdot 10^{-8}$ mol/dm³, respectively. The linear ranges expressed in terms of ΔE_{\max} are similar and equal to cu. 5 mV except for the lowest c_{I_2} value, approaching the Eq. P. region of the titration curve. Possible reasons for this exception will be discussed later. The parameters of the regression equation $\Delta E_{\max} = am + b$ were determined and the correlation coefficient r was always greater than 0.999 for points in the linear range. The linear dynamic ranges calculated as $\log(m_{\max L}/m_{DL})$ are presented in Table I, where $m_{\max L}$ is the maximum mass for which the deviation from linearity does not exceed 5% and m_{DL} is the detection limit for $\Delta E_{\max} = 2$ N. The courses of the $A = f(m_s)$ curves, where A denotes the peak area calculated as $\Delta E_{\max} \times b_{1/2}$ (peak width at half height), are analogous, and their slopes correspond to the mass sensitivity of the detector (see eqn. 11) which is also presented in Table I. Additionally, bearing in mind that $w' = cv$, concentration sensitivity values were also calculated for a gas flow-rate in the detector, v_g , equal to 150 cm³/min. These values are important for the evaluation of the cell as a continuous monitor of SO₂. Absolute detection limits, $m_{DL}/b_{1/2}$, were determined for different compounds and/or under different chromatographic conditions. Since all the sensitivities and detection limits in Table I are based on the slopes of the A vs. m_s calibration curves, the relative confidence limits of such slopes for $P = 95\%$ are shown in Table I for the evaluation of the precision and reproducibility. The following conclusions can be drawn from the values:

- (1) detector sensitivity is well reproducible under the given operation conditions (for the final version of cell, only v_g and h)
- (2) since calibration data were collected over 2-week periods either with or without changing the electrolyte solution, it can be concluded that the concept of large total volume significantly prolongs the electrolyte lifetime
- (3) sensitivity does not depend significantly on the furnace temperature and/or oxygen amount (when samples are mixtures containing SO₂) because the same values were obtained when changing these two parameters.

Preliminary evaluation has indicated that the detector does not introduce any significant peak deformations. Tailing was observed only in a few cases (also for injections of SO₂) and, therefore, can be ascribed primarily to the chromatographic conditions. Detailed numerical analysis of the peaks recorded has shown that normal distribution (even in the absence of tailing) is only an approximation. This problem is being studied further at present,

The same calibration data were employed for calculations of the function $Y = f(m_s)$, where $Y = c_{I_2} \int_0^{\tau_0} \{1 - \exp [K\Delta E(\tau)]\} d\tau$ (see eqn. 10). As shown in Fig. 4, all points (excluding those at the lowest iodine level) fit the same straight line in the investigated range of m_s . Although only twelve points are illustrated, a correlation

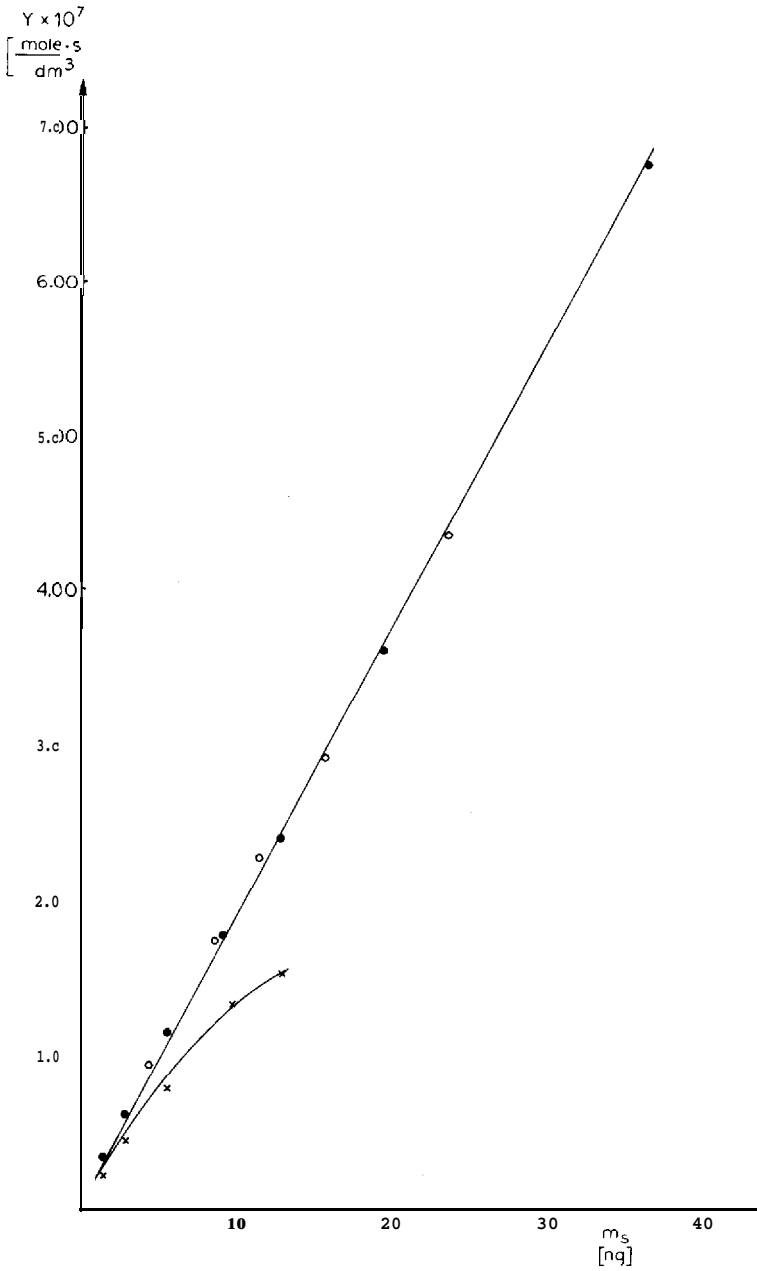


Fig. 4. Linearization of the calibration curves shown in Fig. 3; $Y = c_{12} \int_0^{t_0} \{1 - \exp [K\Delta E(\tau)]\} d\tau$

coefficient, r , of 0.9992 was obtained for $n = 30$ data obtained on different days and for different c_{I_2} values. This shows the correctness of the theoretical considerations regarding the detector signal. Calculations of m_s on the basis of eqn. 10 gave a slope of m_s (calculated) vs. m_s (injected) equal to ca. 0.8. The reason for this is probably that the integrals were calculated on the assumption of a normal distribution of the signal, thus introducing the error connected with this approximation and "losing" the tail area. The obtained result suggests, however, that employment of a more precise numerical model for signal linearization and/or its on-line application can lead to absolute results. The exception at the lowest iodine level (also the atypical deviation from linearity in Fig. 3) can be explained by incomplete absorption for a c_{I_2} value approaching the Eq. P. region of the titration curve.

The behaviour of the detector in combination with a mineralization furnace (for organosulphur compounds) will be described elsewhere. It should be mentioned, however, that even the injections of several milligrams of common organic solvents, e.g., saturated and aromatic hydrocarbons, ethers, esters and ketones, did not result in any signal distinguishable from the noise level, thus permitting the statement that the S/C selectivity ratio is at least 10^6 .

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REFERENCES

- 1 D. M. Coulson and L. A. Cavanagh, *Anal. Chem.*, 32 (1960) 1245.
- 2 D. M. Coulson and L. A. Cavanagh, U.S. Pat., 3,032,493 (1962).
- 3 F. C. A. Killer, *Instrum. Org. Elem. Anal.*, *Anal. Org. Mater.*, 13 (1977) 161.
- 4 J. Ševčík, *Chromatographia*, 4 (1971) 102.
- 5 S. I. Krichmar and W. E. Stiepanienko, *Zh. Anal. Khim.*, 24 (1969) 1874.
- 6 W. E. Stiepanienko and S. I. Krichmar, *Zavod. Lab.*, 10 (1971) 1200.
- 7 W. E. Stiepanienko and S. I. Krichmar, *Zh. Anal. Khim.*, 26 (1971) 147.
- 8 T. Kojima, M. Ichise and Y. Seo, *Bunseki Kagaku*, 20 (1971) 20.
- 9 T. Kojima, M. Ichise and Y. Seo, *Talanta*, 19 (1972) 539.
- 10 T. Kojima, Y. Seo and J. Sato, *Bunseki Kagaku*, 24 (1975) 772.
- 11 T. Kojima, M. Ichise and Y. Seo, *Anal. Chim. Acta*, 101 (1978) 273.
- 12 K. F. Blurton and J. R. Stetter, *J. Chromatogr.*, 155 (1978) 35.
- 13 D. M. Coulson, *J. Gas Chromatogr.*, 3 (1965) 134.
- 14 R. C. Hall, *J. Chromatogr. Sci.*, 12 (1974) 152.
- 15 R. J. Anderson and R. C. Hall, *Amer. Lab.*, 12 (1980) 108.
- 16 O. Piringer and M. Pascalău, *J. Chromatogr.*, 8 (1962) 410.
- 17 P. Jones and G. Nickless, *J. Chromatogr.*, 73 (1972) 19.
- 18 D. F. S. Natusch, T. M. Thorpe, *Anal. Chem.*, 45 (1973) 1184A.
- 19 M. L. Selucky, *Chromatographia*, 5 (1972) 359.
- 20 S. Gluck, *J. Chromatogr. Sci.*, 20 (1982) 103.
- 21 D. C. White, *Anal. Chem.*, 38 (1977) 1615.
- 22 M. C. van Grondelle, F. van de Craats and J. D. van der Laarse, *Anal. Chim. Acta*, 92 (1977) 267.
- 23 M. C. van Grondelle, P. J. Zeen and F. van de Craats, *Anal. Chim. Acta*, 100 (1978) 439.
- 24 M. C. van Grondelle and P. J. Zeen, *Anal. Chim. Acta*, 116 (1980) 335.
- 25 W. Chrzanowski, W. Janicki and R. Staszewski, *Polish Pat.*, 129188 (1983).
- 26 D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, Holt, Rinehart and Wilson, New York, 1969.
- 27 L. Meites (Editor), *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963.