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Short Communication

A MICROCOULOMETRIC METHOD FOR THE DETERMINATION OF NANOGRAM AMOUNTS OF SULPHUR IN ORGANIC COMPOUNDS

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The determination of sulphur in organic compounds is often time-consuming and complicated. The micro-analytical method of Schöniger [1] is simple and precise, the sulphur being determined as sulphate after destruction of the sample in an oxygen flask; many modified procedures of end-point indication have been reported [2—5], and for the determination of traces of sulphur spectrophotometric titrations have been used, but generally, these methods are insufficiently sensitive for trace analysis [6—10].

Coulometric procedures in combination with electrochemical end-point indication are fast, sensitive and more selective [11—20]. Continuous destruction of the sample in a quartz tube is used in most of these methods; either a reductive or an oxidative method can be used.

The drawbacks of the reductive method are that: (a) halogens and nitrogen are reduced to compounds which interfere in the determination of hydrogen sulphide, and although this problem can be solved [20], the determination then becomes too complicated for routine analyses; (b) because of the high reduction temperature (*ca.* 1150 °C), the lifetime of the quartz tube is limited; and (c) it is difficult to find a catalyst which combines a high reducing activity with a low adsorbing capacity for the reduced products.

The oxidative procedure is therefore generally preferred. In this method, any nitrogen oxides formed during the oxidation interfere in the iodimetric determination of sulphur dioxide; Wallace *et al.* [20] solved this problem simply by adding sodium azide to the electrolyte in the titration cell. Another problem is that the conversion of sulphur to sulphur dioxide is non-stoichiometric, sulphur trioxide being formed also. Mixtures of SO_2 and SO_3 exist in an equilibrium which can be described by:

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$$K_p = \frac{p_{SO_2^2} \cdot p_{O_2}}{p_{SO_3^2}} \quad (1)$$

where p denotes the partial pressures of the respective gases. K_p depends [6] on the absolute temperature (T) according to:

$$\log K_p = 6.38 \log T - 9480/T - 0.0049\ T - 5.41 \quad (2)$$

The value of K_p increases from 0.7 at 800 °C through 2.1 at 900 °C to 6.0 at 1000 °C, so that high temperatures are preferred for the oxidation. In addition to the temperature and the partial oxygen pressure, the design of the combustion tube affects the percentage of sulphur converted to SO_2. The tube must be constructed so that the emerging gases are cooled to room temperature as fast as possible in order to "freeze" the equilibrium. Accordingly, both the combustion and the outlet zone temperatures are 950 °C; the emerging gases then cool in the short distance between the tube outlet and the titration cell.

Experimental

Instrumentation. A block diagram of the instrument is shown in Fig.1. The coulometer used is based on the principles described by Krijgsman *et al.* [21, 22] modified to meet the particular demands of the sulphur determination. The electronic diagram is shown in Fig.2. This coulometer was preferred because of its simplicity, low cost and reliability compared to commercially available instruments of the same sensitivity and versatility. The amplification

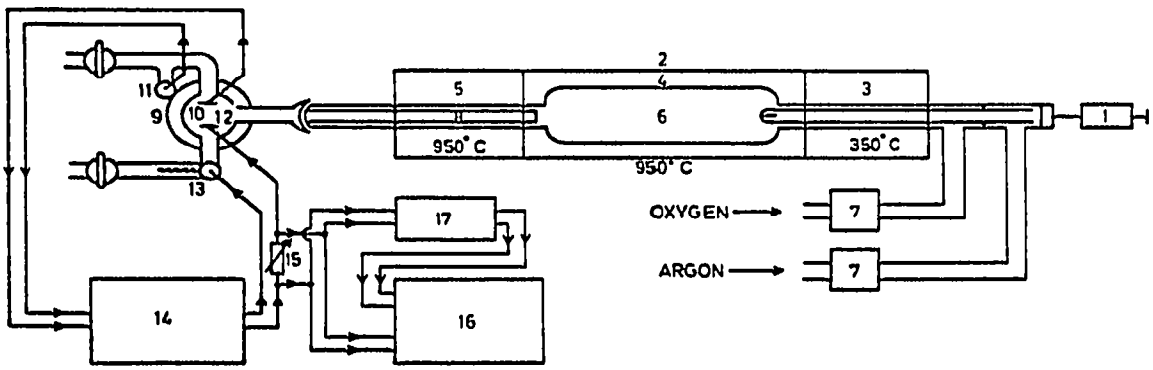

Fig.1. Block diagram of the instrument. 1, Injection syringe, S.G.E. 10A-RN-GP. 2, Furnace, Dohrmann S-300. 3, Inlet zone. 4, Destruction zone. 5, Outlet zone. 6, Combustion tube, Dohrmann P/N 523729. 7, Molecular sieve 5 A. 8, Quartz outlet tube. 9, Titration cell, Dohrmann T-300-P. 10, Indicator electrode, Pt (7 × 7 mm). 11, Reference electrode, Pt wire in saturated I_3^- solution. 12, Generator anode, Pt (7 × 7 mm). 13, Generator cathode, Pt wire. 14, Coulometer. 15, Range-ohm potentiometer. 16, Recorder, Varian A-25 double trace recorder. 17, Integrator, Becker 763. 18, Pressure valve.

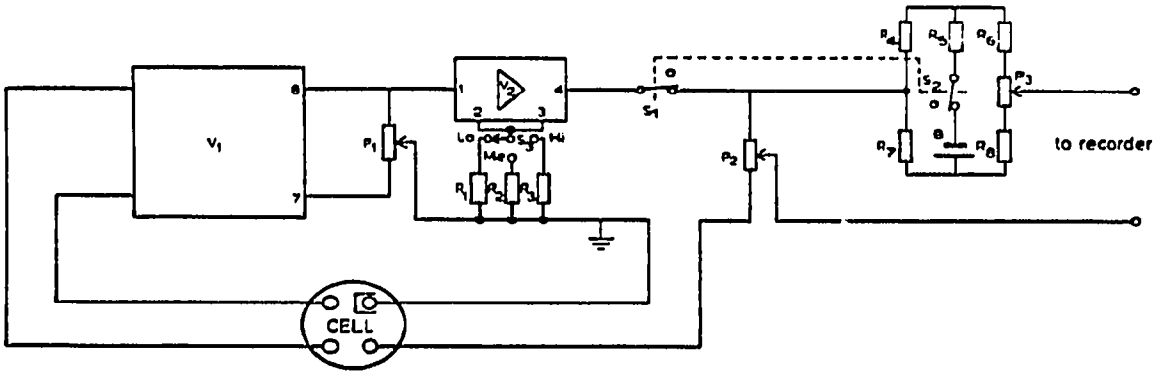

Fig.2. Electronic diagram of the coulometer. V_1, Knick "Messzusatz" type 47. V_2, Knick d.c. amplifier type Hv. S_1, "Function"-switch. S_2, "Function"-switch. S_3, "Gain"-switch. P_1, Potentiometer 10 Ω lin, "Gain set". P_2, "Ten turns" potentiometer 1000 Ω lin, "range-ohms". P_3, "Ten turns" potentiometer 100 Ω lin, "Recorder-zero". R_1, Resistor 1000 Ω, 1/2 W. R_2, Resistor 100 Ω, 1/2 W. R_3, Resistor 10 Ω, 1/2 W. R_4, Resistor 100 Ω, 1/2 W. R_5, Resistor 27 kΩ, 1/2 W. R_6, Resistor 100 Ω, 1/2 W. R_7, Resistor 100 Ω, 1/2 W. R_8, Resistor 100 Ω, 1/2 W. B, Mallory Duracel mercury battery, 1.4 V.

factor can be altered by setting the "Gain" switch as follows: "Lo", 0—0.75 μA output current per mV input signal; "Me", 0—7,5 μA output current per mV input signal; "Hi", 0—75 μA output current per mV input signal. Within each gain set, the amplification can be linearly varied with the "Gain-set" potentiometer.

Reagents. Reference solutions were prepared for the following sulphur compounds: dichlofluanid and parathion (Bayer); tetrasul, tetrasulfoxide and tetradifon (Philips-Duphar); malathion (American Cyanamid Company); promazine.HCl (Wyeth); chlorpromazine.HCl, promethazine.HCl and levomepromazine (Specia); perphenazine (Schering). The solvent is discussed below.

A stock solution of the generator electrolyte was prepared by dissolving 0.2 g of NaI, 20 g of NaBr, 5 g of glacial acetic acid and 6 g of NaN_3 in twice-distilled water and diluting to 1 l. Daily, 5 ml of this solution was diluted with 45 ml of twice-distilled water for actual use.

Procedure. The sample solution (5 μl) is injected with a 10-μl syringe into the inlet zone of the combustion tube. The vapors formed are carried with argon into the combustion zone where the material is burned after addition of oxygen. The products are then swept into the titration cell through the inlet capillary. The titration cell contains the indicator and the generator electrode systems, and is filled with the generator electrolyte containing definite concentrations of triiodide and iodide representing a "bias potential". The SO_2 is oxidized according to the overall reaction:

$$2\,H_2O + SO_2 + I_3^- \rightleftharpoons SO_4^{2-} + 4\,H^+ + 3\,I^-$$

The triiodide concentration is detected by the platinum indicator electrode, the reference platinum electrode being placed in a saturated triiodide solution

in the conventional manner. When the indicator system detects a potential different from the preset bias potential, the generator system operates until the potential is restored to the initial value. The total current that passes through the generator system is integrated, so that the amount of sulphur present in the sample can be calculated.

The optimal working conditions are: oxygen flow, 125 ml min^{-1}; argon flow, 175 ml min^{-1}; inlet zone temperature, 350 °C; combustion zone temperature, 950 °C; outlet zone temperature, 950 °C; range-ohms, 500 Ω. The injection rate must not exceed 0.2 $\mu l\ s^{-1}$, otherwise incomplete combustion will occur.

Special care must be taken in choosing the solvent; it must be sufficiently polar to dissolve the sulphur compounds, and its boiling point should be high enough to avoid selective evaporation of the solvent in the injection needle. A 5:2·5:2·5 (v/v) mixture of hexadecane, acetone and petroleum ether proved satisfactory.

Results and discussion

In the generator electrolyte, iodide and triiodide are kept low, to minimize evaporation of iodine and to ensure maximal sensitivity; bromide serves as a redox buffer in order to obtain a quantitative yield of triiodide, and as a charge carrier in order to maintain a low cell impedance. The triiodide concentration is a function of the bias potential; a potential of 65 mV was found to be optimal. Deviations from this value resulted either in excessive evaporation of iodine or in a slow reaction rate. The stirring rate must be as fast as possible without damaging the titration cell components.

The amplification factor must be adjusted according to the following considerations. If it is too low, there is tailing of the titration curve, but if it is too high, there is overshooting; both effects cause extended titration times. In practice an amplification factor varying between 0.35 (samples with high sulphur content) and 0.60 $\mu A\ mV^{-1}$ (samples with low sulphur content) was found suitable. Under these conditions an analysis can be completed in 3—6 min.

The sulphur content of a sample can be calculated by the following equation:

$$S\ (ng\ \mu l^{-1}) = \frac{M\,Q\,10^{11}}{n\,F\,A\,R}$$

where A is the volume injected (μl), M is the molecular weight of sulphur, R is the recovery (%), and n, Q and F have their usual meanings.

The recovery and the linearity of the instrumental response for different sulphur types were determined for prepared standards in the 5—100 p.p.m. range. The results in Table I show that the recoveries averaged 76.0 % and were independent of the type of sulphur linkage. Table II indicates that the percentage recoveries vary with the amount of sulphur, being 78.8 % for 5 ng S μl^{-1}, 76.5 % for 20 ng S μl^{-1} and 74.0 % for 100 ng S μl^{-1}. If a calibra-

TABLE I

The recovery for prepared standards of different sulphur compounds

Sample	S present (ng μl^{-1})		Recovery (%)	No. of detns.	s_r (%)
	Calcd.	Found			
Dichlofluanid	20.0	15.6	77.7	6	1.5
Tetrasul	19.9	15.2	76.5	7	2
Tetrasulfoxide	19.5	14.9	76.3	7	1.5
Tetradifon	20.1	15.4	76.4	8	1.5
Malathion	21.9	16.0	73.1	6	2
Parathion	29.3	23.1	79.0	6	2.5
Promazine.HCl	20.6	15.5	75.2	7	1.5
Chlorpromazine.HCl	18.6	13.9	74.7	5	0.5
Promethazine.HCl	23.5	17.7	75.3	8	1
Levomepromazine	19.8	14.9	75.3	7	1.5
Perphenazine	21.3	16.4	77.0	6	1.5

TABLE II

Variation of recovery with concentration of sample

Sample	S present (ng μl^{-1})		Recovery (%)	No. of detns.	s_r (%)
	Calcd.	Found			
Tetrasul	4.97	3.86	77.7	5	3
Tetrasul	19.9	15.2	76.5	7	2
Tetrasul	92.7	67.5	72.8	11	1.5
Tetradifon	5.02	4.00	79.9	5	5.5
Tetradifon	20.1	15.4	76.4	8	1.5
Tetradifon	87.6	65.9	75.2	9	1

tion curve is prepared, the method can be used to determine 10—500 ng of sulphur in organic compounds. The procedure can be used for the determination of sulphur compounds in surface waters [23].

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