

MICRODETERMINATION OF DITHIOCARBAMATES BY
GAS CHROMATOGRAPHY*

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During previous work at this institute¹, carbon disulphide liberated by the decomposition of dithiocarbamic acid derivatives with hot acid was determined by gas chromatography, using the method of internal normalisation².

This method involved:

- (a) the use of a second component, in this case *n*-heptane, which however gave a rather long retention time (28 min) under the experimental conditions employed;
- (b) the weighing of volatile products;
- (c) the injection of the sample into the gas chromatography apparatus by means of a microsyringe. This is not always easy or reproducible, especially when the materials undergoing quantitative microanalysis possess high vapour pressures;
- (d) the use of an experimentally determined correction factor in calculating the concentration of the product being examined.

It is therefore particularly desirable to replace the absorption of CS₂ in *n*-heptane by condensation of the free CS₂ in a trap immersed in liquid air.

Use of this direct method makes gas chromatography of the CS₂ evolved more accurate and more sensitive, and at the same time overcomes the difficulties listed above.

Elimination of the second component, and hence of any impurities it might contain, is particularly desirable, especially if these impurities include the substance to be estimated³.

In the procedure adopted in the present work, CS₂ obtained from the decomposition of dithiocarbamic acid derivatives by hot H₂SO₄ was collected in a liquid air trap, omitting the intermediate operations. The whole of this condensate was then introduced directly into the gas chromatography apparatus. This method permits the determination of very small quantities of CS₂ (considerably smaller than those which can be with equal ease determined by other methods), according to the sensitivity of the detector and to the accuracy in measuring the areas under the recorded peaks⁴.

The method described below permits the determination, in solutions of various dithiocarbamates, of amounts of CS₂ as low as a few γ , under conditions which eliminate sources of error, such as weighing and sampling by means of a microsyringe.

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EXPERIMENTAL

Calibration curves

The first step was to construct calibration curves for pure CS₂.

Owing to its extreme volatility, pure CS₂ could not be injected directly into the column, since the peak would run off the scale, even if the smallest samples were used and the apparatus was set for the lowest sensitivity.

It was therefore necessary to prepare a number of solutions of CS₂ in *n*-heptane, not by weighing, but by volumetric measurement with a microsyringe. Using 0.005–0.01 ml of these solutions, it was then possible to inject a series of known amounts of CS₂ into the column and to measure the areas under the corresponding peaks.

The results used to prepare the calibration curve, corresponding to a flow rate of the carrier gas equal to 1.5 l/h, are shown in Table I.

TABLE I.

DATA USED TO PREPARE THE CALIBRATION CURVE WITH A FLOW RATE OF 1.5 l/h

CS ₂ concentration (g × 10 ⁻³)	Area under peak (cm ²)
1.261	3.5
2.522	6.6
3.783	10.4
6.305	17.8
11.349	31.6
12.610	35.0
18.915	52.0
25.220	69.6
37.830	104.0
50.440	140.0

The areas, which were measured planimetrically, were obtained under the conditions shown in Table II.

The calibration curve shown in Fig. 1 is suitable for the determination of medium and high concentrations. It cannot, however, be used for low concentrations owing to the irregularity of the peaks obtained, which are dragged out too much by the slowly flowing carrier gas. To obtain regular peaks with areas coinciding exactly

TABLE II

EXPERIMENTAL CONDITIONS

Equipment	Fractovap model B (C. ERBA-MILAN)
Column	2 m length, i.d. 6 mm
Packing	30–60 mesh celite
Liquid phase	25% silicone grease E-301
Thermostat chamber temperature	85° ± 0.2
Carrier gas	He, at 1.5 l/h 3.6 l/h
Bridge current	18 mA
Chart speed	1.25 cm/min
Retention times	9 min 45 sec at 1.5 l/h 4 min at 3.6 l/h

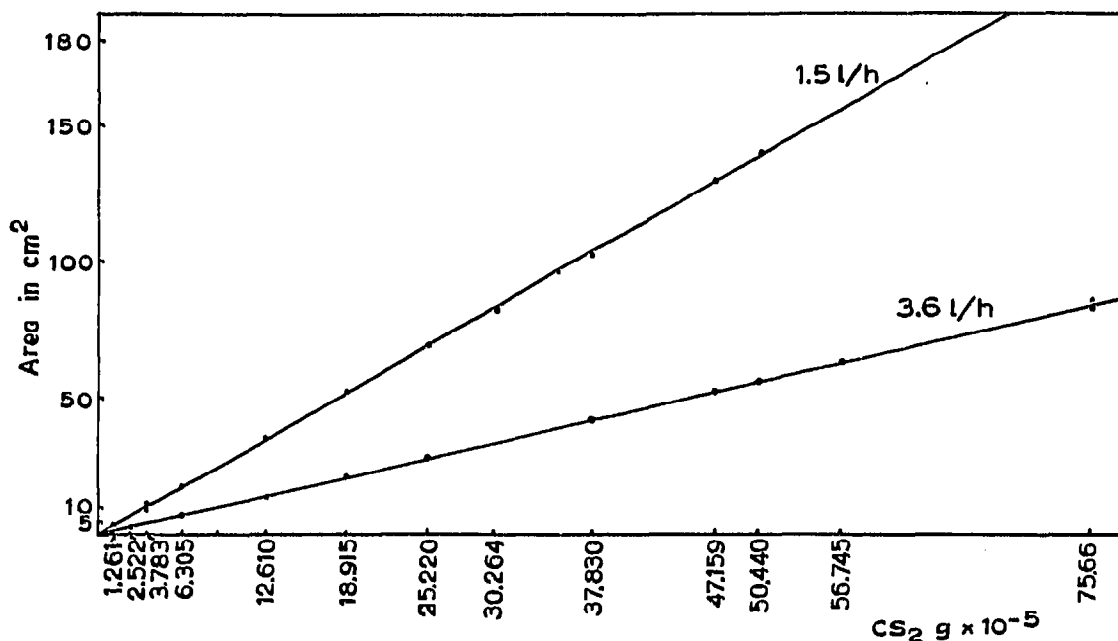


Fig. 1. Calibration curves.

with the calibration curve, the flow rate of the carrier gas was therefore increased from 1.5 to 3.6 l/h for low concentrations of CS_2 .

The new curve, which is also shown in Fig. 1, possesses a less steep slope than the first plot and has the advantage that it can be used for all the concentrations examined. The data used to construct it are shown in Table III.

The experimental conditions mentioned above remained unchanged, except that the rate of flow of the carrier gas was increased from 1.5 to 3.6 l/h, the pressure at the column inlet being equal to 0.27 kg/cm². This change reduced the retention time of carbon disulphide to 4 min.

TABLE III

DATA USED TO PREPARE THE CALIBRATION CURVE WITH A FLOW RATE OF 3.6 l/h

CS_2 concentration ($\text{g} \times 10^{-5}$)	Area under peak (cm^2)
0.448	0.52
2.522	2.8
6.305	7.2
12.610	14.0
18.915	20.8
25.220	28.0
37.830	42.0
50.440	55.6
56.745	63.2
75.660	84.0

Determination of CS_2

The above calibration curves were used to determine, by gas chromatography, the CS_2 , produced from the decomposition of specially prepared pure sodium ethylenebis-dithiocarbamate with hot H_2SO_4 .

This compound possesses the great advantage over the dithiocarbamates of other metals in being water soluble. Standard aqueous solutions could thus readily be prepared, with concentrations ranging from 4 to 12%. Solutions containing various amounts of CS_2 were then prepared by diluting known volumes of these solutions to the required concentrations.

The apparatus used to distil the samples is shown in Fig. 2 on a scale of 1:10. The operation is carried out in a stream of helium (aspirated in directly from a fractometer) in place of air, to avoid any possible oxidation of the products during decomposition and distillation.

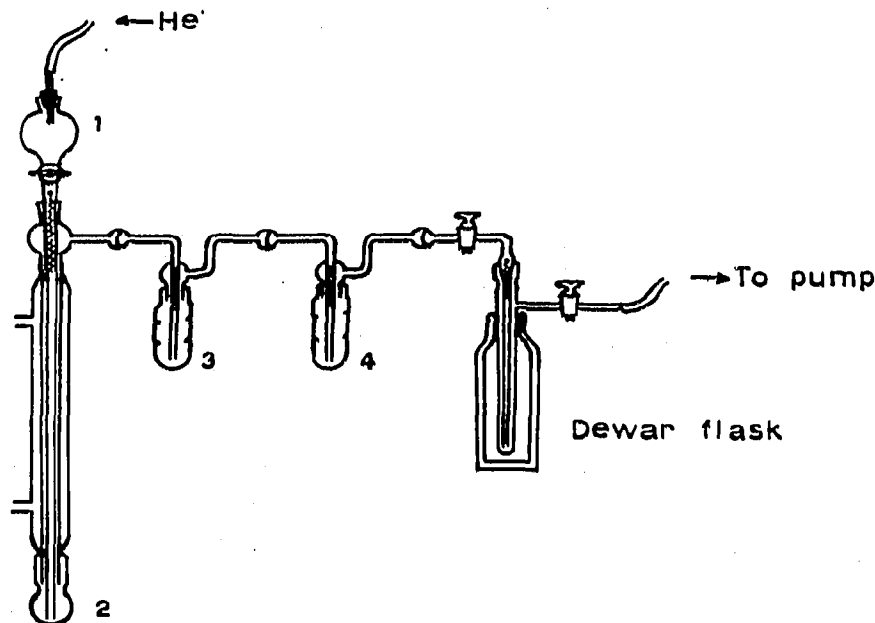


Fig. 2. Apparatus for distillation of CS_2 .

The rate of flow of He must not be too high, and should be 1 l/h. Traps 3 and 4 contain concentrated H_2SO_4 to retain as much as possible of the water vapour evolved in the distillation. The cadmium acetate tube included in Clarke's apparatus to absorb hydrogen sulphide has been omitted, since H_2S has a much shorter retention time and does not interfere at all with the detection of CS_2 .

The cell in which the CS_2 is trapped and solidified by liquid air is illustrated in Fig. 3.

The evaporated sample is introduced into the gas chromatography apparatus by displacing a known quantity from a calibrated container, using the same carrier gas. To ensure that the resultant peaks are regular and significant, and therefore easily measurable, the gaseous sample should be introduced into the adsorption column as rapidly as possible, and without excessive dilution by the carrier gas. The gas will thus occupy the entire cross-section of the column, but will spread over the shortest possible portion of its length. For a column with an internal diameter of 4–8 mm, the volume of the gaseous sample should normally not exceed 5 cc. In the present work it was found that an excessive rate of flow of the carrier gas could be avoided under the existing experimental conditions, and the CS_2 could be displaced

sufficiently rapidly (assuming evaporation from the cell at ambient temperature), if the total internal volume of the cell was 3, or at most 4 cc.

On the other hand, the condensation cell must be at least 15–20 cm long to ensure complete collection of the CS_2 during distillation.

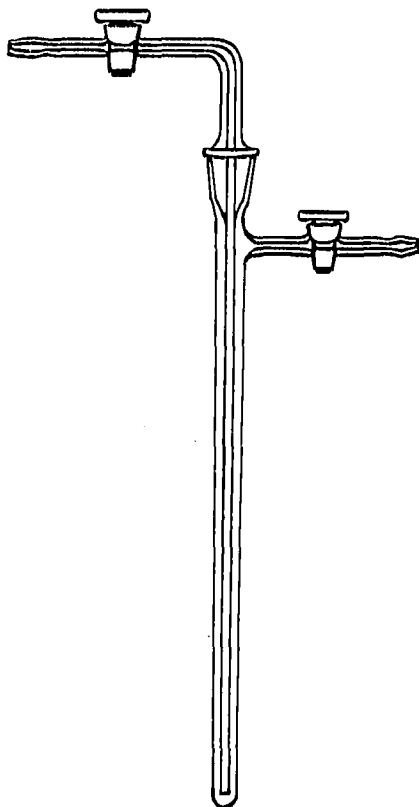


Fig. 3. Trap to collect CS_2 in liquid air.

It is not necessary to know the exact volume of the cell nor the pressure and temperature of the gas retained in it, since all the gaseous products liberated by decomposition and distillation of a known quantity of the initial substance are eventually displaced by the carrier gas and carried into the adsorption column.

The method of carrying out the entire operation in the various stages (decomposition, distillation and introduction of the condensate into the column) is as follows. The required volume of the solution to be examined is introduced into flask 2, and 10–20 ml of 1.1 *N* sulphuric acid, previously heated to its boiling point, are placed in funnel 1. The funnel is then closed with a stopper through which passes the inlet tube for helium from the fractometer. Slight suction is then started using the pump, and the flow is adjusted by means of a Mohr clip to the desired velocity as soon as all the acid has passed into the flask. The solution is immediately heated to 100°, so that the liquid begins to boil evenly as soon as possible.

After 50 min distillation, the taps of the cell containing the condensed CS_2 and other possible volatile products are closed, the cell is removed from the Dewar flask, and is immediately attached via a suitable adaptor to the manifold for the introduction of the sample into the chromatographic column (Fig. 4).

It is very important that this operation should be completed fairly quickly,

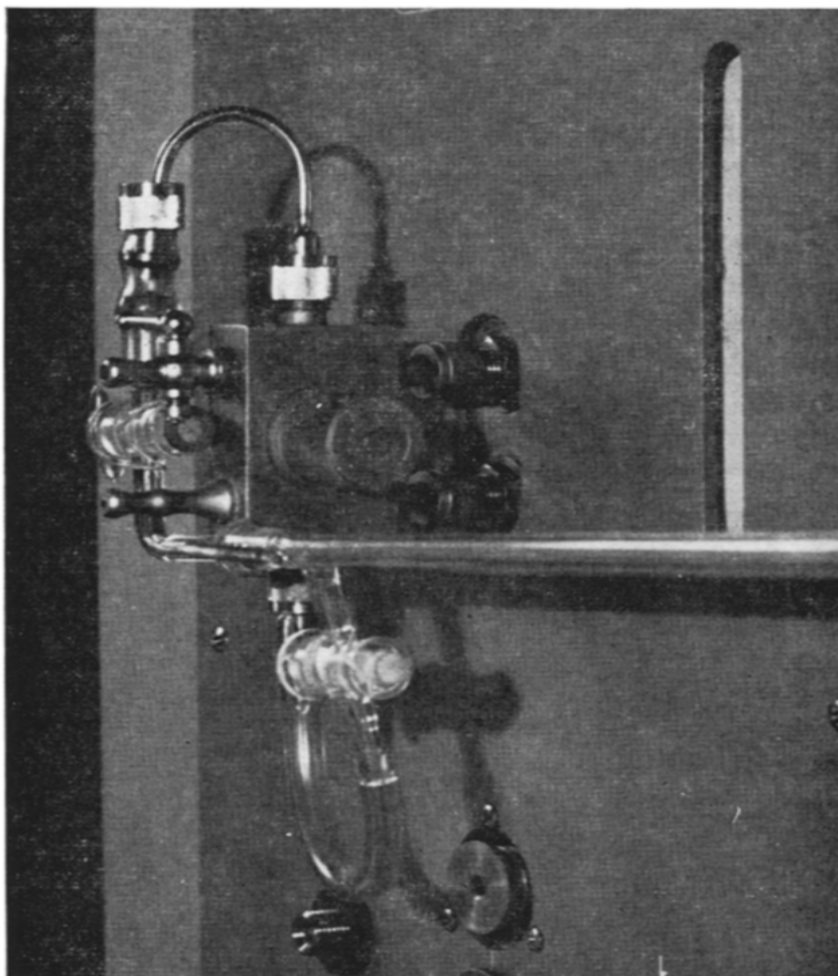


Fig. 4. The manifold for the introduction of samples.

since the stream of helium which is to carry CS_2 into the column must be connected while the cell is still very cold, to avoid evaporation of any water condensed in the cell. Introduction of water vapour into the column would give rise to a peak close to that of the CS_2 , so that the latter could not be perfectly zeroed.

If, on the other hand, the temperature of the cell remains too low, the CS_2 may not be completely vaporised. It is therefore advisable to allow the cell to warm up for 2 min after its removal from the Dewar flask before the carrier gas is passed in. About 1 min after connecting the carrier gas, the CS_2 cell is again cut off from the analytical system, to avoid contamination of the column with evaporating water.

Disregarding the limits of sensitivity of the apparatus and of the planimetric measurements, it can be stated with considerable confidence that the method does not give appreciable errors.

In addition to the work with pure water-soluble sodium dithiocarbamate, the method was also tried out on the corresponding zinc, manganese, and iron salts. Since these are insoluble in water, very dilute aqueous suspensions of these compounds were prepared, adding a few drops of a wetting agent (polyglycol esters) to facilitate the dispersion process.

In contrast to the use of the same dithiocarbamates suspended in inert diluents, or to the use of the solid product alone, the addition of a wetting agent enabled the control tests to be carried out on quantities of the order of a few γ , by reliable volumetric sampling, and with perfectly reproducible results.

It can be seen from Table III that with the aid of the procedure described it is possible to determine quantities of dithiocarbamates corresponding to less than 5 γ of CS_2 , even if the parent compounds are rich in impurities and do not dissolve in water. Control experiments with pure products gave, even at lower concentrations, perfectly reproducible results which were practically identical with theoretical values.

Ethylene-bis-dithiocarbamic derivatives tend to give side-reactions which effectively reduce the quantity of CS_2 evolved by the production of other sulphur compounds, such as ethylenethiourea and H_2S . To avoid this source of error it is imperative to carry out the distillation at 100° throughout.

Having eliminated interference directly associated with the final processes of evaluation of CS_2 , the conversion to CS_2 of even extremely small amounts of organic dithionic compounds, irrespective of their composition and nature (provided they contain the $-\overset{\text{S}}{\text{C}}-\text{S}-$ group which can be converted to $\text{C}\ll\text{S}$), can be controlled by controlling the conditions under which the starting materials are decomposed.

SUMMARY

Carbon disulphide obtained from the acid decomposition of pure and commercial dithiocarbamates and bis-dithiocarbamates was entrained in a stream of helium and condensed in a trap immersed in liquid air.

The entire condensate was then analysed by removing the trap from the liquid air and connecting it directly to an appliance for introducing gaseous substances into a gas chromatographic column.

The experimental procedures for preparing the calibration curves and for the determination of the compounds in question are reported, and advantages of the proposed method are described. One of these advantages is that, besides eliminating any risk of interference which may be encountered in other methods, this technique enables amounts down to a few γ of carbon disulphide to be determined.

With the aid of the method described it is therefore possible to determine quantitatively trace amounts of dithiocarbamates, or of any compounds which can liberate carbon disulphide.

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