A NEW QUANTITATIVE INTEGRAL DETECTOR FOR GAS CHROMATOGRAPHY

THE "BRUNEL" MASS INTEGRAL DETECTOR

S. C. BEVAN AND S. THORBURN

Department of Chemistry, Brunel College, London (Great Britain)

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The international adoption of gas chromatographic methods makes the establishing of universally acceptable quantitative standards a matter of special importance. Although quantitative analysis by gas chromatography can be a method of high precision and accuracy, often exceeding those of alternative methods in those cases where alternative methods are available, the attainment of high accuracy may demand time-consuming measurement of zone areas[1,2] as well as calibration of the detector for molecular response[3–10]. These requirements are in addition to those of representative sampling and injection, a stable partition system, a linear detector[7,11,12], and a reliable recorder. Whilst the whole question of quantitative gas chromatographic analysis is complex, the kind of detection system available does much to determine the approach made to any particular problem.

The requirements[13–20] to be met by a useful detector include: high sensitivity, wide applicability, stability, rapidity of response, adaptability to automatic recording, safety, ease of construction, economy, robustness and, a point of special importance in quantitative analysis, a response directly related to some fundamental property such as mass, so that calibration for every sample component and for varying conditions of operation is unnecessary. No single detection system has yet been devised which satisfies all of these demands, and in practice the selection of a detector is determined by the relative importance attached to the various demands listed above.

The progress of gas chromatography during the past ten years has been marked by the invention of a considerable number of different detectors, designed to respond to changes in various physical or chemical properties of the column effluent gas. A limited number of these detectors have been successful in establishing themselves in practice; a successful detector owes its acceptance to its ability to meet some only of the requirements conspicuously well. Thus, the integral titrimetric method of JAMES AND MARTIN[21], and the gas volumetric method of JANAK[22] have the virtues of integral measurement but are of very restricted application. SHAKESPEAR'S katharometer[23], MARTIN'S gas density meter[24,25] and SCOTT'S hydrogen-flame detector[26] have proved their worth in commercial chromatographs. These three detectors are useful at concentrations in the intermediate range, down to about one part in 10^6 of carrier gas, that is, with column loads of about 1 mg. The gas density meter requires only a knowledge of molecular weights for simple calibration. The argon detector of

LOVELOCK[27] and the hydrogen flame ionization detector of MCWILLIAM[28] are conspicuous for extreme sensitivity. Capable of detecting concentrations of solute smaller than one part in 10^{10} of carrier gas, they make possible column loadings of as little as a fraction of a microgram, but they require calibration for molecular response and, like all the other detectors mentioned excepting the first two, they furnish a differential chromatogram.

The advantages of high sensitivity detectors are generally recognized[19]; they are of particular value in the analysis of scarce materials and in the selection of optimum operating conditions. However, with diminishing sample size, errors independent of the detection system may dominate the attainable accuracy of the results[29,30]. The introduction of a predetermined amount of a representative sample becomes more difficult, the spread, purity and reactivity of the stationary phase may complicate or even vitiate the quantitative interpretation of the chromatogram. Further, the effective inertness of the support may no longer be presumed, and the quality of the carrier gas may become more critical.

The recent heavy emphasis on high sensitivity of detection, coupled with corresponding improvements in column efficiency[31,32], has elevated gas chromatography to the status of one of the most sensitive of all methods of analysis. This concentration of attention and effort on microanalytical aspects may well be responsible for some overlooking of the merits of less sensitive detectors, and may have helped to obscure the possibility of other lines of development. It is remarkable that no success appears to have been achieved in applying what must be, in principle at least, the simplest and most direct of all possible methods of detection, namely, the direct continuous weighing of the sample components as they emerge from the column.

We have established the feasibility of a mass integral detector of this kind. By passing the effluent gas from the column through a suitable absorption vessel mounted on a balance, the change in weight brought about by the arrival of absorbable gas or vapour may be observed directly, or may be made to operate a continuous chart recorder. The integrams obtained in this way provide ready quantitation by measurement of the step-heights.

Although so simple in principle, the integral mass detector offers certain important advantages over most of the established detection systems. Since it is the fundamental property of mass which is being measured, molecular response factors are not involved, and no calibration or calculation is necessary in obtaining the gravimetric composition of the sample. Moreover, the need for an integrator[33–36], always an expensive item and not always a reliable one, is eliminated.

In most of our experiments with the mass detector we have used samples in the range 1–20 mg, but we see no reason why this method of detection should not be employed with samples as small as, say, 20 μg, or, at the other extreme, as large as are used in preparative gas chromatography.

EXPERIMENTAL

In our preliminary experiments on mass detection we tried the fairly obvious method of bubbling a fine stream of the column effluent gas through a quantity (about 20 ml) of an involatile solvent, such as di-octyl phthalate, contained in a glass weighing-bottle mounted on the pan of a direct-reading, air-damped analytical balance. The

results of these first tests were highly encouraging, although the success was incomplete. Stepped chromatograms were, indeed, obtained, but they suffered from two serious faults: first, the step-heights did not correspond to the known weights of the sample components, but were about 20% low; and second, the weight of the absorption system did not remain constant after each absorption, but showed a steady decline following the absorption of each component. The first fault was due to the buoyancy effect of the absorber liquid on the gas inlet tube which, being fixed, was immersed to a depth which varied with the vertical movement of the balance pan during the experiment. The second fault was due to loss, by volatilization, of dissolved components after their initial absorption.

Corrections for these two faults could, however, readily be applied to the recorded weights of the absorption system, and mass integrams could then be plotted. Fig. 1 shows such a corrected mass integram for a mixture of ether, acetone and chloroform separated on a 300 × 6 mm column of 60–80 BSS Celite with 15% polyethylene glycol adipate at 20°, the absorber liquid being di-octyl phthalate.

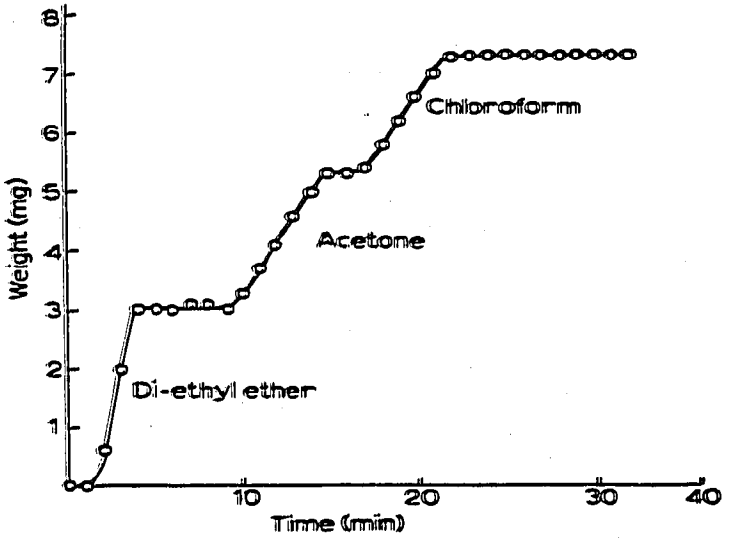

Fig. 1. Mass integram from standard analytical balance (corrected masses).

The feasibility of direct mass detection having thus been established, attention was directed in the next experiments to elimination of the faults of the absorber used in the earlier tests. Furthermore, in all later experiments the changes in weight of the absorber system were followed and recorded automatically by a recording balance (Stanton Automatic Thermo-Recording Balance, Model TR-01).

Buoyancy effects were eliminated by avoiding contact between the gas inlet tube and the absorption liquid in the absorber. The effluent gas from the column, instead of being made to bubble through the liquid, was made to pass close to a layer of liquid lining the interior surface of the absorber. In order to ensure efficient absorption, woven glass cloth, impregnated with absorber liquid, was used to provide a large area of absorbing film.

Errors of the second type, *i.e.*, loss of dissolved component by volatilization from the absorber, were eliminated, as far as many different kinds of samples are concerned, by replacing the simple solvent used in the preliminary tests by a chemi-

cally reactive absorber which, instead of merely dissolving physically the components as they reached the absorber, reacted chemically with them, thus fixing them in a form exerting very low vapour pressure, so that loss by vaporization was negligible. Thus, acidic substances in the column effluent gas were absorbed by solid sodium hydroxide or potassium hydroxide, or by concentrated solutions of these in an involatile solvent such as ethylene glycol. Another chemical absorber of very general usefulness is concentrated sulphuric acid. This effectively absorbs not only amines, but also alcohols, ethers and ketones forming with them, by proton donation, -onium ions of the types: R_3NH^+, ROH_2^+, R_2OH^+ and R_2COH^+. We are currently studying the efficiency of absorption of cooled active charcoal.

A simple form of the mass integral detector, (conveniently referred to as the "Brunel" detector), is shown in Fig. 2. The gas stream from the column is carried into the absorption vessel by a capillary connector of up to 0.5 mm internal diameter and about 12 cm in length. Provided that the diameter of the connector is kept small,

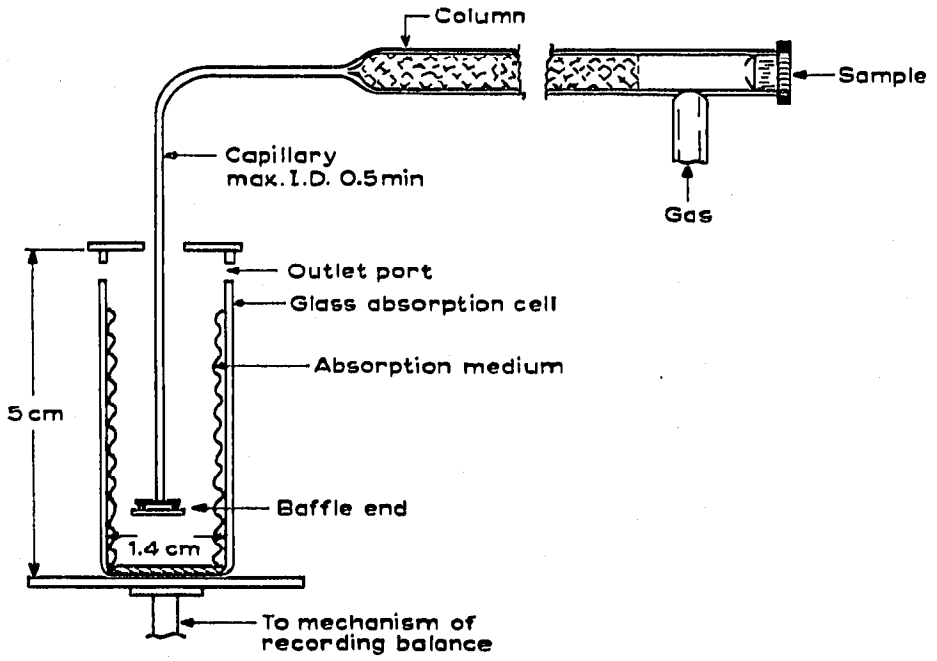

Fig. 2. Mass detector—simplex design.

the length appears to have negligible effect on the resolutions obtainable. The capillary ends in a baffle plate which deflects the stream of gas against the sidewall of the absorber, thus aiding absorption and minimizing the effect of the gas stream on the balance, in the direction of movement of the balance pan. The carrier gas, stripped of its absorbable components, emerges from the absorber through the capillary inlet port, or through side ports. Our experiments indicate that in the cases of amines, alcohols, ethers and ketones, absorption by concentrated sulphuric acid is quantitative, and that these components, once absorbed, are not lost by volatilization. The accuracy obtainable in these cases is determined by the sensitivity of the balance rather than by the absorber. A typical integral chromatogram, obtained using a sulphuric acid absorption cell, is reproduced in Fig. 3. Sample: 3.8 mg; column: 100 × 0.3 cm; support: alkali-treated Celite 80–100 BSS; stationary phase: 10% polyethylene

glycol 400; temperature: 20°; gas-flow: 25 ml nitrogen per minute. Such integrams represent the attainment at the milligram level of an ideal expressed by Dr. A. J. P. MARTIN[20,37] at the 4th International Gas Chromatography Symposium in Hamburg, June 1962, at which a preliminary announcement of our work was made.

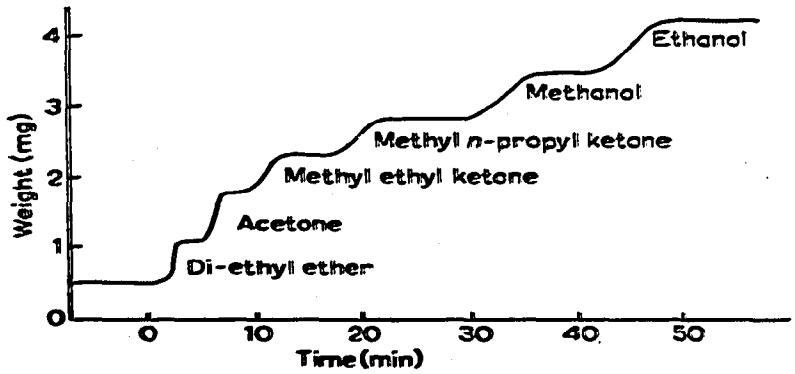

Fig. 3. Mass integram from recording balance.

Development work in progress includes detector design, extension of mass detection to the microgram range, including the use of electrobalances of the Cahn or Sartorius types, and the possibilities of selective absorption.

Patent applications have been made in respect of this invention[38] and rights have been assigned to the National Research Development Corporation.

SUMMARY

The ideal detector for quantitative analysis by gas chromatography would need neither calibration nor the application of integration procedures to a differential chromatogram. This paper describes the experimental realization of a detector possessing these two desirable characteristics. The "Brunel" mass integral detector yields an integral chromatogram in which the absolute masses of the sample components are directly recorded as step-heights.

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