A GAS DILUTION SYSTEM FOR CONTROL OF DETECTOR RESPONSE IN GAS CHROMATOGRAPHY

N. L. GREGORY

National Institute for Medical Research, Holly Hill, Hampstead (Great Britain)

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INTRODUCTION

Detectors used in gas chromatography have sensitivities which vary according to the compound being detected, and only seldom, *e.g.* for the gas density balance[1], is it possible to predict the nature of the variation from readily available independent data. The form of the variation is often of considerable interest and a correlation between sensitivity and chemical structure may provide information regarding molecular structure as well as clarifying aspects of the mechanism of detection[2–4]. This is particularly true of the electron capture detector[5]; relative electron capture coefficients, sometimes loosely called "electron affinities", of many compounds are being studied with the aim of correlating electron capture with chemical reactivity and physiological properties[6,7].

In such a study it is necessary to make comparative sensitivity measurements, and there are two general experimental methods. Thus detector output readings can be determined for known loads of sample applied to the column. For this purpose the compounds to be tested must be available in measurable quantities and in a state of reasonable purity. A more widely applicable method is to correlate the detector output directly with the concentration of sample leaving the column as indicated by a second detector of known quantitative response.

Difficulties arise when the sensitivities of the two detectors differ widely and in some circumstances their working ranges do not overlap at all. As it is impractical in such cases to pass the sample through both detectors at the same concentration, samples leaving the column at sufficiently high concentrations for the one detector must be diluted before entering the other. Small dilution factors can be achieved by adding gas to the total effluent from the column but, where the required factor is large, this leads to excessive gas flows. A novel technique has therefore been developed for taking a small sample of controllable size from the column outflow and adding it to an independently chosen flow of diluting gas.

EXPERIMENTAL

An electron capture detector[8] was mounted in a small oven and connected to the output of an existing gas chromatograph (Fig. 1) in which the detector was a gas density balance[9]. Between the two detectors was placed a gas flow splitting device, shown in more detail in Fig. 2. This was connected initially as shown by the broken line in Fig. 1, *i.e.* the dilution flow did not pass through the "pulsator".

In adjusting the apparatus the pump speed was set, by the needle valve (NV 1), to give a convenient gas flow (E, Fig. 2) into the detector; *e.g.* with the scavenge flow set at 180 ml/min[8] and a pumping rate (P) of 210 ml/min the flow (E) into the detector would be 30 ml/min. The dilution flow (D) was then adjusted by the second needle valve (NV 2) to be nearly equal to this amount, leaving a small quantity (δC) to be

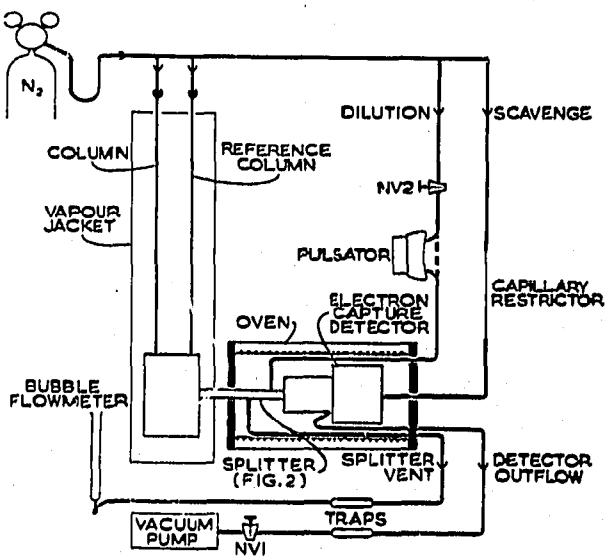


Fig. 1. The gas flow splitter interposed between a gas density balance and a high-temperature electron capture detector.

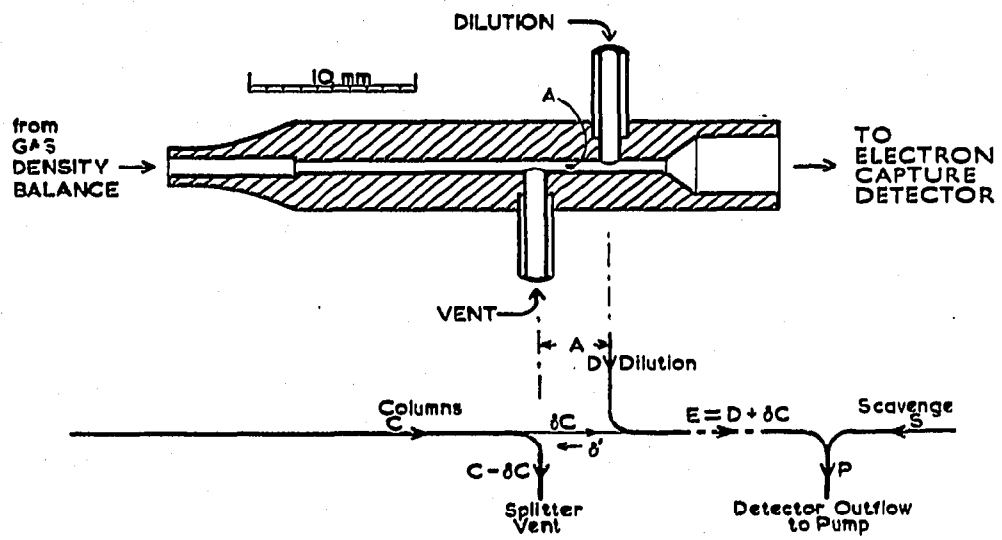


Fig. 2. (Upper) The gas flow splitter; to scale. Section (A) of capillary 1.06 mm diameter, 4.4 mm long. Dilution input pipe 1.4 mm I.D., 140 mm long. (Lower) Gas flow paths. Sample passing to detector = δC, $\delta C = P - (D + S)$ and is set by adjustment of P and D. δ' shows reversed direction of mean flow when using pulsator.

drawn in from the columns. The remainder of the column flow passed through a trap (Fig. 1) and a flowmeter to waste. Thus, by suitable adjustment of NV 2, δC could be chosen to be *e.g.* 1.5 ml/min and, with the figures quoted, the gas entering the electron capture detector would contain sample at 5% of the concentration leaving the gas

density balance. The proportion of the sample leaving the column which eventually entered the electron capture detector was determined by the ratio between δC and C, the total gas flow leaving the gas density balance; *e.g.* with a sample column passing 100 ml/min and a reference column passing 50 ml/min, and the other settings as above, only 1 % of the sample would enter the detector. Flow rates measured at the splitter vent were used to calculate approximately the dilution ratio at any setting of the apparatus, although absolute figures were not required for the present purpose.

In developing this method of dilution the following points were considered important:

(1) It was economical in gas, only a small proportion of the sample being actually diluted.

(2) At no point was a fine capillary tube carrying sample, the section at A being sufficiently wide not to block.

(3) The dilution, or splitting, factor was controlled by large pressure drops across elements outside the oven and not carrying sample in significant concentration. The factor was therefore stable with respect to small changes in back pressure, changes in detector temperature and sample concentration.

(4) Only at one part of the system, in the capillary (A), was the gas flow rate small and the volume of tubing here was sufficiently small to cause no significant time delay.

(5) Adjustments could be made without changing gas flow rates in the detector.

It was found necessary to fit the needle valves used (Griffin and George S11–100) with worm drives (Meccano) for convenience in making the adjustments, and to replace the rubber gland washers from the valves with similar ones turned from polytetrafluoroethylene before satisfactory stability could be attained. It was then possible to work conveniently with dilution ratios of the order of 100:1 at room temperature.

At higher dilution ratios, or at higher temperatures, drift proved to be troublesome and stable results could be obtained only over periods of a few hours. The system was therefore modified, as shown by the full lines of Fig. 1, by the inclusion of a "pulsator", a device for making transient reductions in the rate of flow of gas from needle valve (NV 2) into the flow splitter.

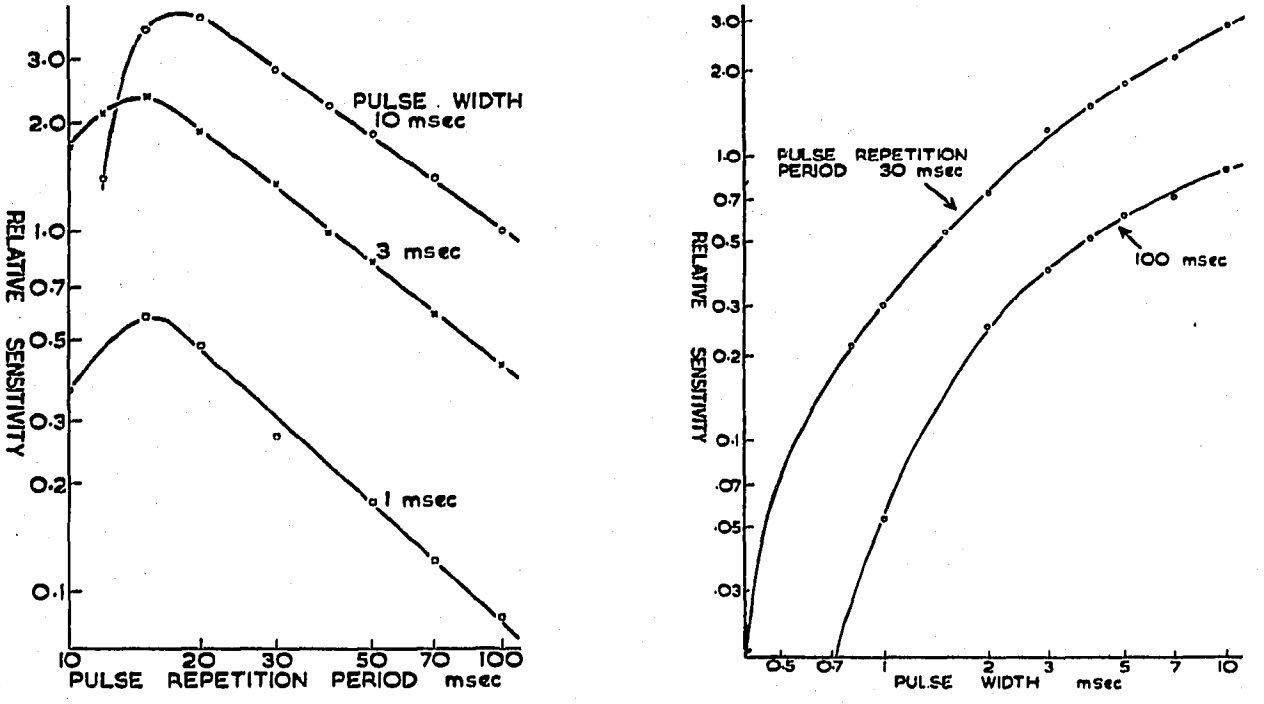
The pulsator was constructed by connecting pipes into a headphone earpiece with epoxy resin, and sealing the diaphragm with a polythene gasket and, externally, with silastomer, thus forming a gas-tight cavity in the dilution gas stream, with the diaphragm as one wall. When an electrical pulse was fed to the magnets of the headphone the movement of the diaphragm caused a transient reduction of pressure in the cavity and hence a transient reduction in the gas flow rate to the flow splitter. This in turn caused a compensating increase in flow through the section (A) of the capillary, so maintaining the constancy of flow (E) to the detector.

The needle valve (NV 2) was now readjusted to make the mean flow in the dilution line (*i.e.* through NV 2) slightly greater than that taken by the pump, thus reversing the mean flow through the capillary (A). Sample from the column flow entered the electron capture detector gas flow system only during the pressure pulses provided by the electrical system. As these were short, well spaced, rectangular pulses, *e.g.* with a width of the order of 3 msec and a repetition period of 100 msec, sample was flowing into the detector for only a small fraction of the time, and splitting was achieved in proportions that depended very largely on the characteristics of the electrical pulses rather than on a delicate balance of gas flow rates.

The gas flowed through a sufficiently large cavity (about 0.3 ml) between the splitter and the active volume of the detector to ensure that considerable mixing took place. It could thus be regarded as a continuous sample, rather than a series of pulses, as it entered the detector.

RESULTS

The way in which the detector response was controllable by electrical adjustment of the pulse width and pulse repetition frequency is demonstrated by Figs. 3 and 4, in which the sensitivity of the detector and splitter, regarded as a unit, is compared with an arbitrary standard setting; a relative sensitivity of unity corresponds to a dilution factor of approximately 1.6 %. Smooth control was, in fact, achieved over a range of sensitivities of rather greater than 100:1, *i.e.* from about 6 % to below 0.06 %. In this range the dilution ratio was not critically sensitive to the value of pulse voltage (Fig. 5) provided that this was sufficiently large. The range of dilution factors could be extended



Figs. 3 and 4. Effective sensitivity as a function of pulse width and pulse repetition period. Square pulses of peak height 100 V. Dilution factor at relative sensitivity of 1 = 1.6 %.

in either direction by changing the pump speed (NV 1) and making corresponding changes in dilution flow (NV 2), thus altering the gas flow to which the sample was added.

The flexibility of the system is demonstrated by the chromatograms of Fig. 6. Curve (a) is a chromatogram of a mixture of chlorinated methanes taken from the gas density balance record. Curve (b) is the corresponding simultaneous chromatogram from the electron capture detector operated, in this case, with a constant dilution roughly appropriate for comparison of the chloroform peaks in the two records. The other peaks in the electron capture record are not accurately measurable. On repeating

the chromatogram, with an identical load but this time with a progressive increase of dilution, the electron capture chromatogram (c) was obtained. All of the peaks were now measurable.

The dilution factor achieved at any one setting has been sufficiently stable for

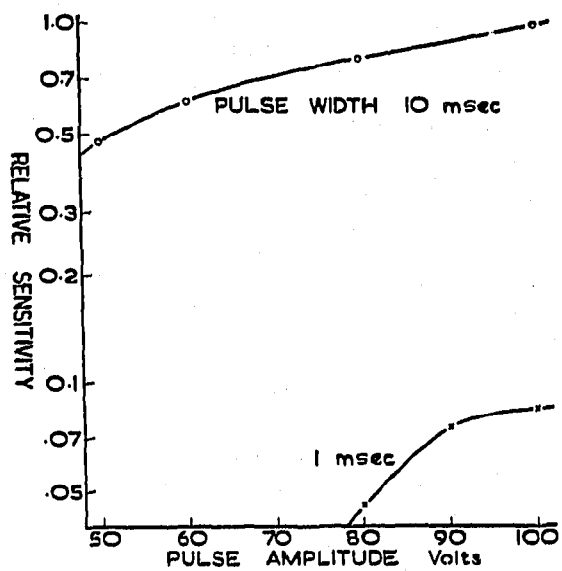


Fig. 5. Effective sensitivity as a function of pulse voltage. Pulse repetition period = 100 msec.

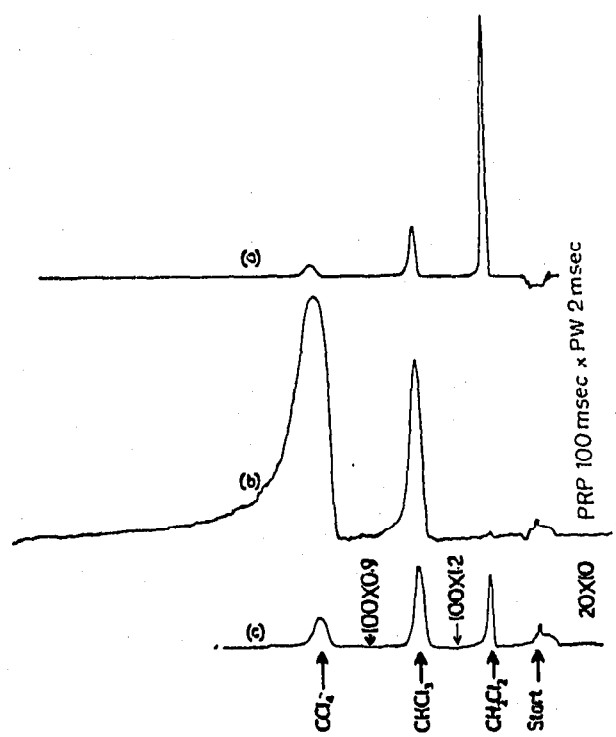


Fig. 6. Chromatograms demonstrating that suitable conditions can be chosen for measurement of a wide range of compounds. (a) Gas density balance chromatogram of mixture CH_2Cl_2–$CHCl_3$–CCl_4 approx. (20:5:1, v/v). Total load 0.25 μl. (b) Simultaneous electron capture record at constant dilution. Detector temperature 69°. PRP = pulse repetition period; PW = pulse width, both in msec. (c) Repeated electron capture record with progressively adjusted dilution.

spontaneous changes to be masked by detector sensitivity changes due directly to variations in temperature, and detector calibration curves have been prepared using many test substances, *e.g.* chloroform[8].

DISCUSSION

The practical value of the technique lies primarily in that it provides a dilution system which can be used to reduce the sensitivity of a detector by a stable factor. By combining the two methods described above, *viz.* sampling the column effluent using the vacuum pump with or without the pulse system, the factor can be chosen to be anywhere within the range 1:1 to 1:2000.

It is demonstrated (Fig. 3) that the reduction in sensitivity is inversely proportional to pulse repetition period (PRP), as would be expected, provided that the PRP is greater than about 25 msec. The effect of a change in PRP in this range is therefore calculable. Fig. 4 shows, however, that the observed sensitivity varies non-linearly with respect to pulse width, changing more rapidly than pulse width when this is less than 1–2 msec, and less rapidly when it is more than 3–4 msec. This, again, is to be expected as the square pulse applied to the diaphragm can result in a square pressure pulse in the headphone cavity only when the pulse is short compared with the time required for the gas flow to compensate the depression caused by the diaphragm displacement. There is thus an upper limit to the pneumatic pulse width which can be generated in the earpiece. Once a pressure change has been generated in the headphone cavity, it takes a definite time to reach the flow splitter, and short pulses are further shortened and attenuated in the process of their propagation to the splitter. The sensitivity of the detector–splitter combination thus falls more rapidly than the electrical pulse width. With the apparatus constructed the two effects overlap and there is no region in which the effective pneumatic pulse in the splitter is of the same duration as the electrical pulse applied to the diaphragm, and therefore no region where the dilution factor can be calculated from the applied pulse. All measurements can, however, be made relative to a standard sample, or the apparatus can be calibrated at selected settings of the pulse width control.

It is probable that a wider range of control, with a more linear relationship between dilution factor and electrical pulse width, could be achieved with apparatus designed specifically for pulsed gas flow, with a wider, shorter tube from the pulsator to the splitter, without rubber connections, and with a high acoustic impedance at the gas input side of the pulsator. A shorter length of capillary bore at A might also be an advantage. The lower limit of the pulsator range might be extended by the same means and possibly also by using a moving coil transducer, instead of the moving iron headphone, and driving it electrically with ramp waveforms instead of square waves. In its present form, however, the apparatus has been proved suitable for studies of groups of compounds of widely differing electron capture properties by comparative methods.

The facility with which the detector sensitivity can be changed, simply by switching the pulse width or repetition frequency, makes it convenient to measure constituents of widely different electron capture coefficients in a mixed sample, *e.g.* mono- and dichlorobiphenyls occurring in the same reaction mixture can be studied in one chromatogram. This method has the advantage over the alternative procedure, *viz.*

control of amplifier gain, that load size can be chosen to make peaks due to inactive compounds large enough, compared with noise level, to be measurable without overloading the detector by more active compounds; but calibration of the splitter is, of course, necessary at each of the settings used.

The same method may be useful in other applications, *e.g.* detection of trace constituents using conventional detectors, where similar difficulties occur, and a further application is in preparative chromatography. Here it is not always desirable to pass the whole sample leaving the column through the detector, and various sampling systems have been tried. The present system has advantages in that large split ratios can be achieved without the use of fine capillaries and the ratio should not be critically dependent on back pressure caused by the collector. It is also expected to be a suitable system for sampling process streams for chromatographic analysis.

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SUMMARY

A technique is described for controlling detector response by variable splitting of the gas flow leaving a chromatograph column. This gives, in effect, a detector of variable sensitivity and allows direct comparison to be made between a highly sensitive electron capture detector and a gas density balance of lower sensitivity but with a known response.

The pneumatic pulse technique devised should also be applicable to other problems, *e.g.* trace analysis, preparative chromatography or process stream sampling.

REFERENCES

1 A. J. P. MARTIN AND A. T. JAMES, *Biochem. J.*, 63 (1956) 138.
2 J. C. STERNBERG, W. S. GALLAWAY AND D. T. L. JONES, in N. BRENNER, J. E. CALLEN AND M. D. WEISS (Editors), *Gas Chromatography, 3rd Intern. Symp.*, Academic Press, New York and London, 1962, pp. 221–267.
3 G. PERKINS, G. M. ROUSYLAB, L. D. LINDY AND W. C. HAMILTON, in N. BRENNER, J. E. CALLEN AND M. D. WEISS (Editors), *Gas Chromatography, 3rd Intern. Symp.*, Academic Press, New York and London, 1962, pp. 269–285.
4 N. L. GREGORY, *M. Sc. Thesis*, University of London, 1961.
5 J. E. LOVELOCK, *Anal. Chem.*, 33 (1961) 162.
6 J. E. LOVELOCK, *Nature*, 189 (1961) 729.
7 J. E. LOVELOCK, P. G. SIMMONDS AND W. J. A. VANDENHEUVEL, *Nature*, 197 (1963) 249.
8 N. L. GREGORY, *J. Chromatog.*, 13 (1964) 26.
9 E. A. JOHNSON, D. G. CHILDS AND G. H. BEAVEN, *J. Chromatog.*, 4 (1960) 429.