

CHROM. 8493

SOLUTE SWITCHING AND DETECTION BY SYNCHRONOUS DEMODULATION IN GAS CHROMATOGRAPHY

J. E. LOVELOCK

Bowerchalke, Salisbury, Wilts. (Great Britain)

SUMMARY

It is a common practice in physical measurement to use coherent switching and synchronous demodulation for the recovery of weak signals from overwhelming noise. This paper describes a key component, the solute switch, which coherently modulates the solute concentration of the carrier stream. Its use enables the recovery of chromatography signals otherwise lost in noise. Examples of its application in gas chromatography to improve detectivity and to eliminate baseline drift are given.

INTRODUCTION

The sensitivity and performance of the contemporary gas chromatograph usually satisfies its users, so much so, that it is not generally realised that the signal-to-noise ratio of the gas chromatograph is generally far from that which is theoretically possible.

To many in the chemical industry it might seem unnecessary, even subversive, to further increase the sensitivity of a chromatograph equipped with an electron capture detector (ECD). Yet by the application of solute chopping and synchronous demodulation an improvement in the signal-to-noise ratio of at least ten-fold can be achieved. As well as sensitivity improvement there are other benefits, which include the abolition of baseline drift and the possibility of temperature programming even with a single channel.

This paper describes a gas chromatograph with synchronous detection made possible through the use of a new component, the solute switch. Examples of its use in electron capture gas chromatography (GC) are given and the general application of solute switching in GC and liquid chromatography is discussed.

THEORETICAL BASIS

In GC few peaks are narrower than 1 sec and few longer than 500 sec in width. A signal channel with a band pass of 0.01-2 Hz would therefore faithfully transmit nearly all of the signals which a practical chromatographer might encounter. It is not difficult to design and construct amplifier and recording systems in this pass-

band. Noise introduced in the amplifiers and recorders is usually negligible compared with that arising in the chromatograph itself.

Noise in chromatographic signals is conveniently considered in three bands: First, high-frequency noise at levels above 2 Hz; secondly, noise within the chromatograph pass-band of 0.01–2 Hz, and thirdly, low-frequency noise below 0.01 Hz.

The high-frequency noise above 2 Hz includes shot noise in the detector, line frequency interference and electrical transients. All of this noise is routinely reduced to negligible levels by the inclusion of one or more low pass filters. Noise at frequencies below 0.01 Hz is usually referred to as baseline drift. It arises from a number of causes, which include the slow desorption of detectable vapours from the column and the slow attainment of thermal equilibrium and flow-rate equilibrium in the gas chromatograph itself. It should be possible to reduce this low-frequency noise by the inclusion of a well-chosen high-pass filter but this is rarely done.

By far the most intractable source of noise, however, is that distribution which occurs within the GC band itself, namely 0.01–2 Hz. This noise comes from two principal sources:

(1) The detection of slowly desorbing components of past experiments or of column bleed. Usually the frequency of this noise would be less than 0.01 Hz and could be eliminated. In practice, changes in detector temperature or carrier flow-rate can modulate this background signal and cause noise within the GC pass band.

(2) Real detectors sense not only substances but also temperature, pressure and gas flow-rate changes. The frequency of these changes also often lies within the GC pass band. They give rise to noise signals.

The improvement of the signal-to-noise ratio is a common problem in all physical measurements. The only feature unique to GC is how little has been done to take advantage of the well known techniques of signal processing with the notable exception of the correlation methods reported by Smit¹. In spectroscopy, for example, it is commonplace to arrange conditions such that the signal sought is modulated at some chosen frequency but the noise is not. The chosen frequency can then be selectively amplified and demodulated so revealing the original signal largely free of noise. If the special technique of synchronous demodulation is included, the effective band pass becomes extremely small and improvements in the signal-to-noise ratio of 100 times are easily achieved.

Is such an improvement possible in chromatography? To apply this procedure requires a solute switch. This is a component which, when inserted between the column and detector, will allow the carrier to flow unimpeded but can remove or not remove, as the case may be, the solute from the carrier stream. Ideally when the switch is on, all of the solute is instantly removed and when the switch is off none of it is removed. If the switch is driven on and off at a frequency which the detector can follow, the signal from the detector will now be modulated with an a.c. component at the switching frequency. This may then be amplified in a narrow band pass a.c. amplifier and synchronously demodulated. A signal will be revealed which does not include noise outside the very narrow band pass of the chopping frequency. Detectivity is enhanced and baseline drift all but completely eliminated. Fig. 1 illustrates the assembly of components needed to achieve this result.

This procedure alone provides conspicuous advantages but in chromatography a further bonus comes from the possibility of making the switch itself selective for a

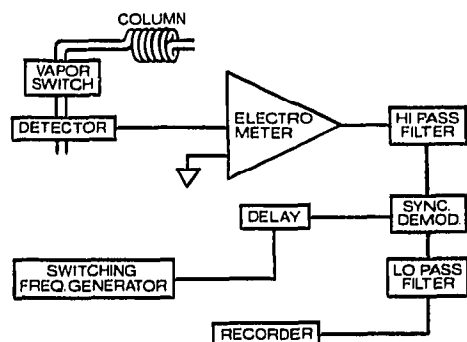


Fig. 1. Block diagram illustrating the connection of components for a chromatograph with solute switching and synchronous demodulation.

chosen component or a chosen component class. In such an event a general purpose detector, such as the flame ionisation detector, can be made selectively sensitive for a specific compound or class of compounds. The advantages already mentioned are still available but in addition the presence of a trace component buried in a large excess of detectable materials is now specifically revealed.

EXPERIMENTAL

Solute switches

Two solute switches were used. The first was a coulometric ECD² which almost completely ionised and destroyed electrophilic compounds. This detector was switched between the destruction and the free passage of solute, simply by changing the applied potential from 0 to 15 V positive. At 0 V electrons accumulated within the detector to a level sufficient to react with and remove the solute molecules. At 15 V positive they were so rapidly removed that their steady-state concentration was reduced close to zero. The detector dimensions and construction are illustrated in Fig. 2. It contained an ionising source of titanium titride which set free 1.9×10^{11} electrons per second from nitrogen at standard temperature and pressure, equivalent to an ion current at saturation of 35 nA. This detector ionised 99% or more of most strongly electron-attaching substances at carrier gas flow-rates up to 50 ml/min.

The second switch used was made from 10 cm of 0.5-mm-diameter palladium-gold alloy tubing. This was coiled in a helix 3 cm long \times 1 cm in diameter and was totally immersed in water. This switch was operated by heating ohmically to ap-

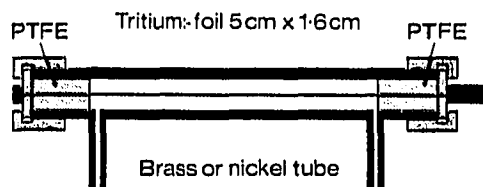


Fig. 2. Construction of the electron capture solute switch.

proximately 500° by the passage of 50 W of ohmic electrical heating; when hot, compounds which were labile decomposed. The water surrounding the coil served to cool it rapidly during the off periods. Since the average heating rate was sufficient to keep the water gently boiling, the switched temperature during the off periods was 100°.

Chromatography

Chromatography was conventional, experiments were made with a series of halocarbons including members which ranged from the strongly electrophilic to the weakly electrophilic and from the thermally labile to the thermally stable. The compounds and the relevant properties are listed in Table I. The stainless-steel column was 2.4 m long \times 6 mm I.D. It was filled with 12% OV-101 on 100–200 mesh Chromosorb W. Samples were introduced either from the gas phase through a 5-ml sample loop or from solution in hexane by syringe injections. For most experiments the column temperature was 40° and the carrier flow-rate 50 ml/mm. Oxygen-free nitrogen was the carrier gas used. The vapour signal was sensed by a second coulometric ECD connected after the switch. This detector was operated using a fixed pulse period of 250 μ sec. The detector output was filtered to remove the pulse frequency and the potential developed across a 500 M Ω input resistor amplified by a unity gain electrometer and then by a unity gain high-pass active filter set to attenuate at frequencies lower than the switching frequency.

Synchronous demodulation

The system employed to process the switched signal is illustrated in general form in Fig. 1. In practice three quite different synchronous demodulators were tried but they all shared a common switching supply. This was a square-wave generator capable of operating over the range 0.1–10 Hz and with an output amplitude of 20 V. It was used directly with the ECD switch and as a trigger for a triac in the primary of a 50-Hz a.c. low-voltage transformer for the heating coil. A separate signal was taken from the switching oscillator through a delay circuit to the demodulator. This delay was adjusted to match the time lost during the flow of gas between the switch and the detector.

System 1. Fig. 3 shows the circuit employed. The filtered a.c. signal from the detector was split into two components 180° apart in phase. The level of these two signals was sampled sequentially and synchronously at the switching frequency by

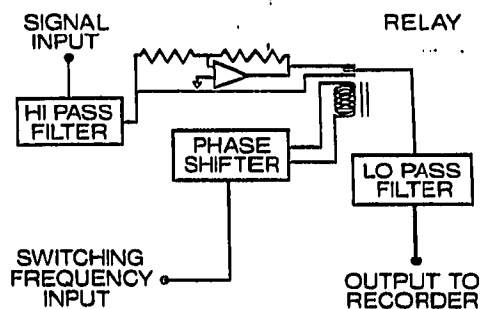


Fig. 3. Simple circuit used to demonstrate the feasibility of the method.

means of a simple mechanical relay driven from the switching generator. The output of the sampling switch was passed through a low pass filter set to remove the switching frequency component and then fed to a potentiometric recorder.

System 2. This employed a professional lock-in amplifier with a Brookdeal Model 9502 phase sensitive detector.

System 3. The filtered a.c. signal was fed via an analog-to-digital converter directly to a Hewlett-Packard Model 9820A computing calculator.

This was programmed according to the algorithm (Fig. 4) to function as a synchronous detector and band pass filter. The output was recorded on a digital XY recorder.

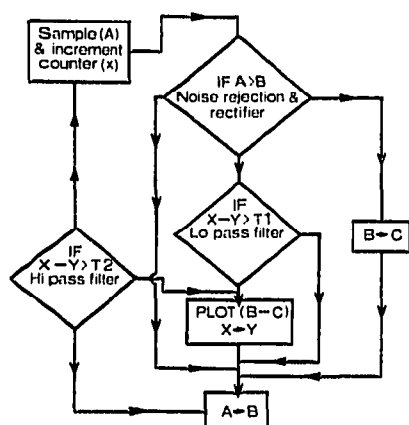


Fig. 4. Algorithm for synchronous demodulation as an "on-line" computer procedure.

Partial switching

So far we have been concerned with compounds which are either wholly destroyed or which pass unchanged through the switch. In practice many substances are only partially decomposed. With these the signal is attenuated as the square of the proportion which is destroyed.

With electron capture the peak area corresponding to a given quantity (Q) of a compound varies with the proportion (p) ionised. The peak area corresponding to the quantity Q is therefore pQ . The a.c. signal from the switched detector signal comes only from that proportion which is ionised and this will be pA , where A is the peak area obtained by conventional electron capture. Since $A = pQ$, the peak area of the synchronously detected signal is p^2Q . The same considerations apply to any other method of destructive switching and this property of the system assures that signals from weakly detected materials are greatly attenuated. This is illustrated in Fig. 5, the chromatogram of the resolution of a trace component, peak A, in air which otherwise would have been lost in the large signals from the excess of the weakly electron-absorbing oxygen.

Other methods

There is no reason in principle why many other procedures such as destruction by ultraviolet radiation, by ionisation using a corona discharge, or by chemical reac-

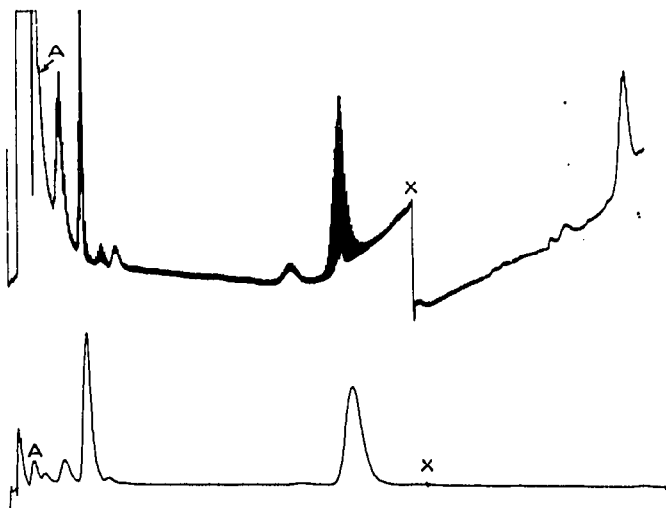


Fig. 5. Analysis of a 5-ml sample of slightly polluted air. Column, OV-101; temperature programmed at 6°/min from 25° to 120°. A manual baseline adjustment is shown at \times . The upper chromatogram shows the detector output normally displayed, the lower chromatogram that after synchronous demodulation. A: Resolution of a peak otherwise lost in the "tail" of the oxygen peak.

tion, could not be used for general or selective switching. The full possibilities of the method, however, probably await the development of a reliable means of switching carrier-gas flow between two or more paths. One of these streams would convey the solute to the detector unchanged, the others would cause it to encounter a means for its change or destruction. It is nearly impossible, for example, to cycle the temperature of the heated switching tube at a rate greater than 1 Hz. To transfer the carrier stream between a hot and a cold tube rapidly presents no such difficulty and the higher the switching frequency the greater the improvement in performance. The transfer of carrier flow between two or more tubes will also make possible the use of selective absorbents, chemical reactors, etc., in the deletion path. These are not easily conceived as direct in-line arrangements.

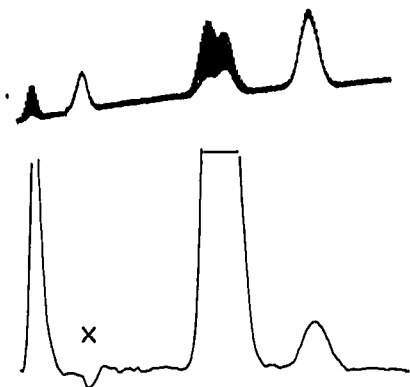


Fig. 6. Chromatogram of a cryo condensed sample of clean air. Note the peak \times , which shows a negative deflection below the baseline. Column, OV-101; temperature, 20°.

TABLE I

COMPOUNDS TESTED AND THEIR RESPONSE TO SWITCHING BY ELECTRON REACTION AND THERMAL DESTRUCTION, RESPECTIVELY

<i>Compound</i>	<i>Proportion deleted</i>	
	<i>Electron switch</i>	<i>Thermal switch</i>
CCl ₃ F	0.95	0
CH ₃ I	0.9	0.9
CHCl ₃	0.01	0.1
CH ₂ CCl ₃	0.1	0.5
CCl ₄	0.98	0.8
CHCl=CCl ₂	0.02	0.01

In the use of the ECD as a switch, it was noticed (Fig. 6) that positive deflections below the baseline can occur. Investigation revealed that this was attributable to the production in the first detector of material detectable in the second. A few compounds, such as dichloromethane, for example, decompose in the first detector and give rise to strongly adsorbing products which may be detected in the second detector. This phenomenon was first reported by Lillian and Singh³. In electron capture analysis this is an interesting or sometimes aggravating anomaly of rare occurrence. The example in Fig. 6 illustrates, however, that synchronous demodulation can be applied to added as well as deleted solutes. Furthermore, where addition occurs it is distinguishable by the phase difference of its effect from deletion. Compounds deleted during the operation of the thermal destruction switch are compared in Table



Fig. 7. Illustration of the enhancement of signal-to-noise ratio. The lower chromatogram shows a direct display, the upper chromatogram that after solute switching and synchronous demodulation. Sample, 5 ml of clean air.

I with those deleted by electron reaction. Otherwise the performance of the two switches did not differ.

DISCUSSION

The signal processing procedures described improve the signal-to-noise ratio in chromatography by a factor of at least 10 (Fig. 7). This is significant in extreme trace measurements but the more important practical advantage of the new procedure lies in its capacity to greatly decrease low-frequency noise components. These include the slowly emerging peaks of unwanted materials and baseline drift from any cause other than a change in the concentration of a strong absorber; the latter usually of course represents a signal. This second advantage is particularly valuable for monitoring applications where equipment is required to function automatically over long time periods. It is valuable also, as the example in Fig. 5 shows, to eliminate baseline drift during the temperature programming of the column.

This preliminary investigation indicates the improvements possible through the application of signal processing methods in one branch of GC. There seems no reason why these advantages should not be available also in other GC detection procedures and in liquid chromatography.

ACKNOWLEDGEMENTS

I am very grateful to my colleagues A. T. Jenkins and L. Machta for their unstinted help and encouragement and for presenting the challenge of the problem.

REFERENCES

- 1 H. C. Smit, *Chromatographia*, 3 (1970) 515.
- 2 J. E. Lovelock, *J. Chromatogr.*, 99 (1974) 3.
- 3 D. Lillian and H. B. Singh, *Anal. Chem.*, 46 (1974) 1060.