APPLICATION OF AN ELECTRON CAPTURE DETECTOR TO THE DETERMINATION OF DIBROMOETHANE IN GASOLINES

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INTRODUCTION

The electron capture detector (ECD) is one of a number of ionisation detectors widely used for monitoring the effluent from gas chromatographic columns[1]. The range of response of an ECD, on a weight basis, covers several orders of magnitude, being very low for saturated hydrocarbons and extremely high, in particular, for polyhalogenated species. In this respect the ECD differs strikingly from other GC detectors which are (within a factor of 2 or 3) insensitive to compound type. Use of an electron capture detector is thus attractive (i) for the determination of small quantities of strongly electron capturing species and (ii) as a means of obtaining qualitative information about components separated by GC. Published applications of electron capture detection relate mainly to the determination of lead alkyls in gasolines[2,3] and of highly halogenated insecticides[4,5]. Although the potential of this detector for qualitative purposes has been noted[1,6] no direct applications have been reported to date.

Dibromo- and dichloroethane are frequently added to gasolines as scavengers, to aid in the removal of lead compounds (arising from the lead alkyl anti-knock agents in gasoline) from engines. All of these gasoline additives can be determined, in principle, using the electron capture phenomenon and the alkyl leads have been determined as mentioned above. However, the relative sensitivity of an ECD to alkyl leads and also to dichloroethane is very much less than to dibromoethane. In attempting to use an electron capture detector difficulties were experienced due to such effects as varying sensitivity and optimum voltage for the same compound from day to day. As a result it has proved difficult to devise a repeatable method for the determination of substances for which the ECD sensitivity is relatively low, such as dichloroethane and alkyl leads.

This paper presents a method for the determination of 1,2-dibromoethane in gasolines. It illustrates the quantitative application of an ECD, and describes some of the experimental problems encountered in its use.

APPARATUS

The oven unit, electron capture detector and their associated electronic equipment were supplied by Gas Chromatography, Ltd., Maidenhead, England. The electron capture detector itself is shown in Fig. 1, the tritium source strength being about
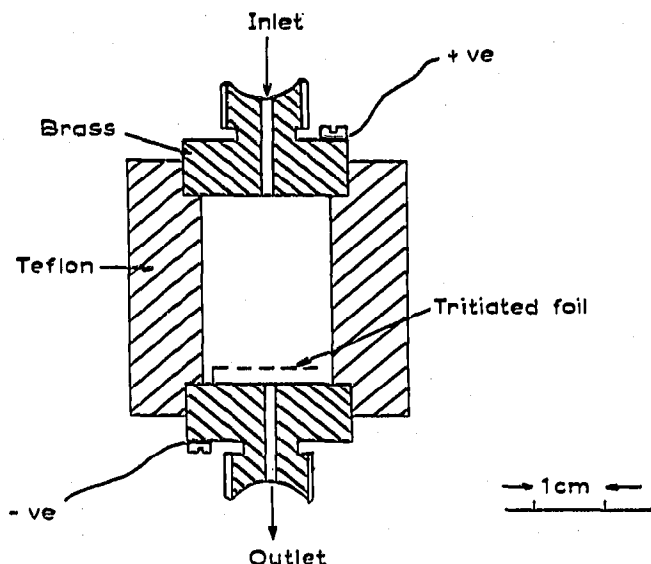
Fig. 1. An electron capture detector.

200 mC. A special "Electron Capture Control Box" permitted the application of any d.c. potential between O and 100 V (to $\pm$ 0.1 V) across the cell.

A 10' by $^1/_4$" inner diameter column packed with 5 % Apiezon "L" plus 0.5 % polyethylene glycol 4000 on "Embacel" was used. The temperature was held at 95°, and the nitrogen carrier gas flow rate was 100 c.c.s. min^{-1}. The carrier gas flow was maintained permanently through column and detector. At the column exit the carrier gas flow was split between detector and waste in the ratio 15:85.

OUTLINE OF THE TECHNIQUE

The determination of dibromoethane (DBE) in gasolines by ECD is a comparatively easy task since the detector response to DBE is many times greater than to any other volatile components present in a gasoline, including the lead alkyls. Indeed the main problem is to reduce the amount of DBE reaching the detector to a level such that the ECD is not completely "saturated".

Gasoline samples were diluted between 25- and 250-fold to bring the DBE content to the range 10–50 p.p.m. by weight, the diluent being 60–80 petroleum ether. A calibration blend of 1,2-dibromoethane in 60–80 petroleum ether, containing about 40 p.p.m. by weight of DBE was prepared and various known volumes of this solution were injected into the chromatograph using a Hamilton syringe (10 μl capacity). A calibration curve of DBE peak height *versus* total amount of DBE injected was thus obtained. The DBE content of unknown samples could then be deduced from the DBE peak height given by a known volume of the petroleum ether diluted sample and its relation to the calibration curve.

DISCUSSION OF THE APPARATUS AND TECHNIQUE

Important parameters to be considered when using d.c. electron capture detectors for quantitative work are:

(a) the potential across the detector
(b) the carrier gas flow rate
(c) the temperature of the detector
(d) the total amount of electron capturing material present in the detector at any instant
(e) possibility of detector contamination.

Detector potential

The variation in detector response with applied potential is shown in Fig. 2. At very low voltages the detector does not respond at all. Above what might be called the "threshold" voltage response increases rapidly to a maximum, falls fairly rapidly to zero and then becomes negative as cross-section, and other, ionisation phenomena take over. Voltages for maximum sensitivity and for the cross-over to
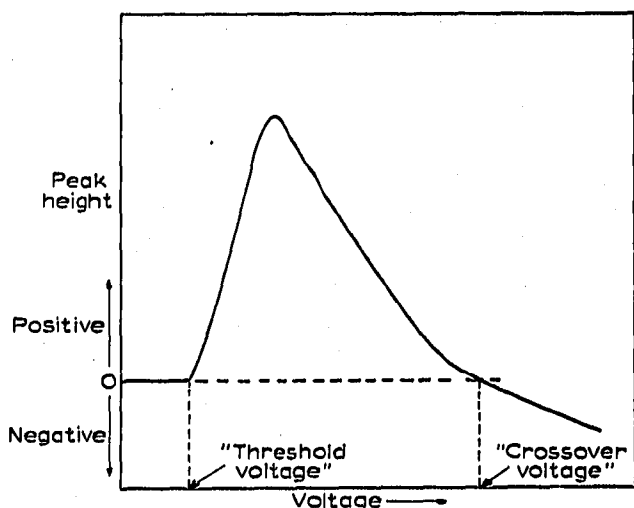

Fig. 2. Electron capture detector. Variation in response with voltage. Temperature 95°.

negative response vary somewhat with compound type. For the present purpose and with the Gas Chromatography Ltd. detector (in which the inter-electrode instance was about 5 cm) a potential of 4 V gave approximately maximum sensitivity to DBE. The very small amount of hydrocarbons of similar boiling point (and, therefore, of similar elution times) present in petroleum ether diluted samples were quite undetectable under these conditions. If, however, there had been interference between DBE and other hydrocarbon components, for example if the DBE levels had been 2 or 3 orders of magnitude lower, it would have been possible to operate the detector at a rather higher voltage (about 7 V). At this voltage hydrocarbons are at, or close to, their "cross-over" point (response becoming negative) and even very large quantities (*i.e.* 10^{-5} moles·sec^{-1}) give zero response whereas DBE is still below its cross-over point, though sensitivity is reduced.

Carrier gas flow

When carrier gas alone is passing through an ECD a steady, standing current flows. The standing current tends to increase with increasing carrier gas flow rate, particularly at low temperatures (Fig. 3). Since entry into the detector of an electron

capturing species leads to a fall in the current the sensitivity and dynamic range of the detector to electron capturing species is likely to increase with increasing standing current. It is therefore useful to operate the detector with a high gas flow rate. In some cases where a low flow rate is needed (*e.g.* for a capillary column) it is desirable to add further nitrogen to the column effluent before it reaches the detector.
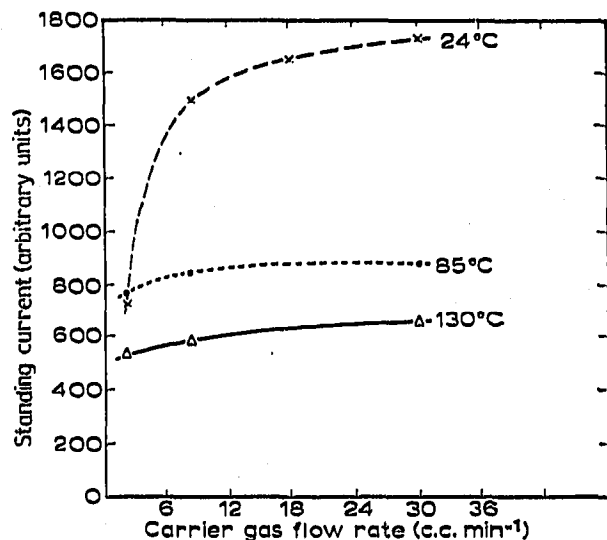

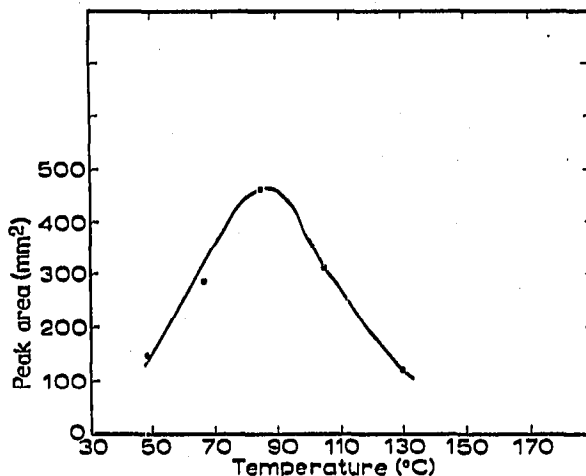Fig. 3. Electron capture detector. Variation in standing current with gas flow rate.

Fig. 4. Electron capture detector. Variation in response with temperature. Sample: 1,2-dibromoethane; voltage: 4 V.

Temperature

It has been found that electron capture detector response is influenced by temperature. Data for dibromoethane are plotted in Fig. 4. Similar response curves have been obtained for other substances. Ideally an ECD should be operated in a thermostated enclosure separate from the column oven.

Quantity of electron capturing material

The ECD functions because electron-capturing materials reduce the standing current. The quantity of electron capturer present in a detector can be so high that all electrons may be captured and no current flows. This occurs if one μl of 1,2-dibromoethane is injected into an ECD, and the detector standing current takes many minutes to recover to its original level. Qualitatively if successively larger quantities of, for example, DBE are passed into an ECD, the peaks obtained have the form shown in Fig. 5. Peak broadening and tailing are seen to be functions of the detector. Peak heights are reckoned from the base line indicated in Fig. 5 (i). In the present state of knowledge it would seem safest to use an ECD only in the range where peak width is constant and peaks are symmetrical. Because of the exponential nature of the capture process calibration is essential.

Possibility of detector contamination

Deposition of relatively involatile material on the tritiated foil of the detector would lead to a serious loss of β-particle emission and consequent loss of sensitivity.

In the analysis of samples which contain relatively involatile components use of a pre-column, with back-flushing facility, is advisable to prevent such components reaching the detector.
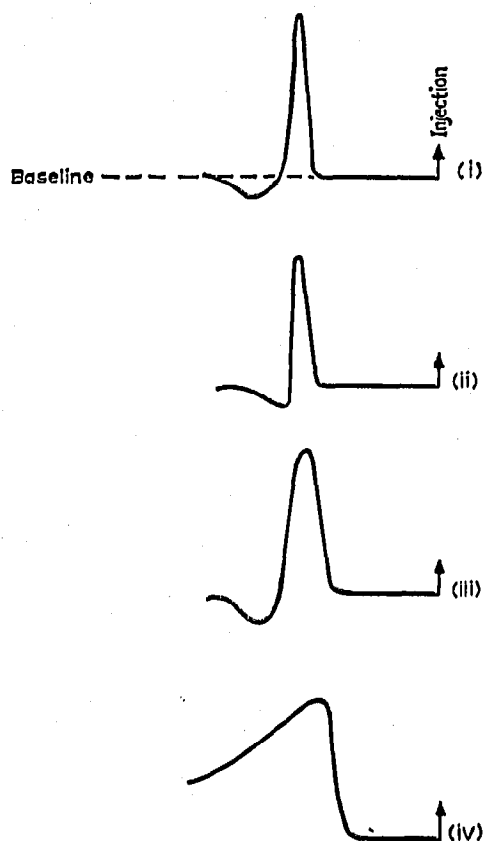

Fig. 5. Influence of quantity on peak shape. The quantity of electron capturing species increases from (i) to (iv).
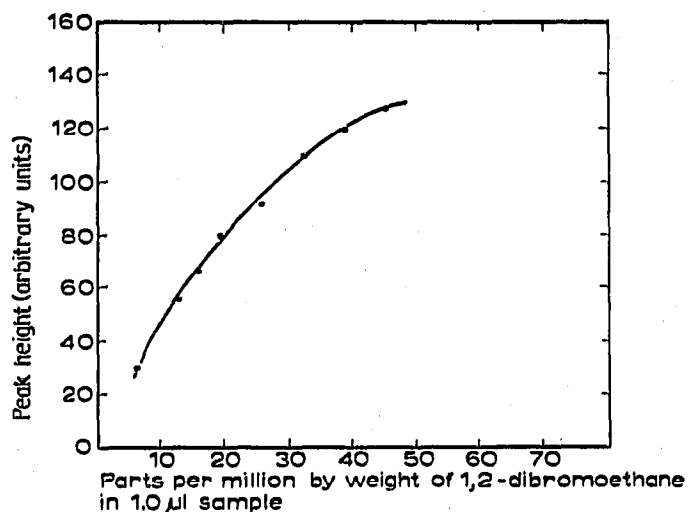
Fig. 6. Calibration curve for 1,2-dibromoethane.

RESULTS

In the foregoing sections the influence of some variables on the determination of 1,2-dibromoethane has been considered. The actual conditions used are set out in Table I. Under these conditions the limit of detection of 1,2-dibromoethane was about $4 \cdot 10^{-13}$ moles·sec^{-1}.

A calibration curve obtained for DBE is given in Fig. 6. In Table II some actual response measurements are given, as measured on a number of days, to show the variation in detector response. When the voltage across an ECD is changed, in the low potential range 1–10 V, the detector takes some time to re-equilibrate as can be seen from the data in Table III. At least 2 h should be allowed before attempting to use a detector after changing the applied potential. The precision of the sample charging (1.0 μl sample size), peak height measurement and detector repeatability operations over a 3-hour period was found, from 12 experiments, to be ±3 p.p.m. at the 32.4 p.p.m. (by weight) level. It is believed that the precision limiting step in this analysis is the sample charging operation.

TABLE I

OPERATING CONDITIONS FOR DETERMINATION OF 1,2-DIBROMOETHANE

Detector temperature: 95°.
Detector voltage: 4 V.
Carrier gas flow rate:
      Column: 100 c.c. min^{-1}.
      Electron capture detector: 15 c.c. min^{-1}.
Column: 10' 5 % Apiezon "L"—0.5 % P.E.G. 4000 on 100–120 mesh "Embacel".
Elution time of dibromoethane: 6 min.
Sample size: 1.0 μl of 60–80 petroleum ether diluted sample, so that DBE concentration is between 1 and 50 p.p.m.

TABLE II

DAY-TO-DAY REPEATABILITY OF DIBROMOETHANE CALIBRATION

Dibromoethane in sample (p.p.m.)	Peak heights (mm)				
	Feb. 6	Feb. 7	Feb. 10	Feb. 11	Feb. 17
6.5	27	36	34	29	30
13.0	52	54	—	—	56
16.2	62	71	—	—	66
19.5	—	61	77	59	80
25.9	100	96	—	—	92
32.4	110	121	118	105	110
45.4	149	—	—	—	128

TABLE III

"EQUILIBRATION" TIME OF AN ELECTRON CAPTURE DETECTOR

Response given by an electron capture detector to a fixed sample charge of DBE (precision of operation $\pm$ 10 % at 2σ level).
Carrier gas flow and temperature had been constant for 5 days but voltage across the cell was changed from 7 to 4 at time zero.

Time zero plus (min)	Peak height (mm)
60	80
105	101
120	110
140	110

SUMMARY

In this paper a method for the determination of 1,2-dibromoethane in gasolines is discussed. The method utilises an electron capture detector which is much more sensitive to dibromoethane than to other gasoline components. The importance of voltage, temperature, total quantity of dibromoethane in the detector and carrier gas flow rate on the performance of the detector is considered. The sensitivity of the detector is $4 \cdot 10^{-13}$ mole·sec^{-1} for 1,2-dibromoethane. The repeatability of the method is $\pm$ 3 p.p.m. at the 30 p.p.m. level.

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