Journal of Chromatography, 319 (1985) 215–217
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,340

Note

Enhanced response of more highly unsaturated lipids on thin-layer chromatography–Iatroscan flame ionization detection after exposing the developed Chromarods to iodine vapour

A. K. BANERJEE
Chemistry Department, Saugar University, Sagar, 470-003 (M.P.) (India)
and
W. M. N. RATNAYAKE and R. G. ACKMAN*
Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, P.O. Box 1000, Halifax, Nova Scotia B3J 2X4 (Canada)
(Received October 29th, 1984)

Aliphatic hydrocarbons are usually expected to give the largest response in gas–liquid chromatography (GLC) with flame ionization detection (FID) due to the presence of only carbon and hydrogen atoms in the molecule[1,2]. This is quite true with GLC–FID, but not necessarily with the flame ionization detector of the Iatroscan[3,4]. It has been speculated that due to radiant heat transfer along the Chromarod surface a part of the more volatile components evaporates before entering the flame proper, resulting in a lower response than would be predicted. Indirect evidence for this phenomenon has been obtained by exposing developed Chromarods to iodine vapour before scanning in the Iatroscan. Aliphatic unsaturated components exposed to iodine gave greater responses than those unexposed.

EXPERIMENTAL AND RESULTS

A mixture of unsaturated lipid standards (squalene, methyl oleate and triolein) in chloroform solution (5 μg of each) was spotted onto cleaned Chromarods-SII. The rods, after humidification in a tank over saturated sodium chloride solution for 10 min[5], were developed in hexane–diethyl ether–formic acid (98:2:1) for 40 min, dried at room temperature for 2 min, exposed to iodine vapours in a glass thin-layer chromatography (TLC) tank for 10 min and then scanned on the Iatroscan. For comparison another set of experiments was carried out with the same mixture of lipid standards applied to the same set of Chromarods. The procedure was the same except that the rods were not exposed to iodine vapour prior to scanning. The exposed set of Chromarods showed an increased response for squalene and methyl oleate relative to triolein. (Fig. 1A and B have been selected for presentation because the triglyceride peaks were identical). Squalene was the most affected material and showed the largest enhancement (at least 70% relative to triolein) after iodine exposure.

It is likely that iodine adds across a proportion of the ethylenic bonds and the iodine derivatives formed have higher boiling points than the original compounds.

0021-9673/85/$03.30

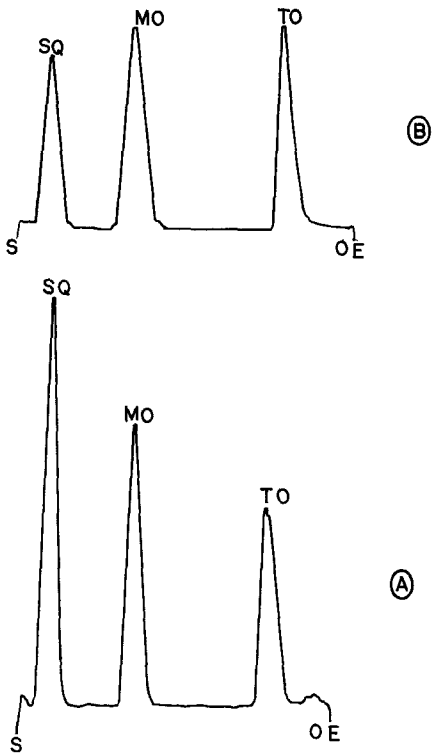

Fig. 1. Comparison of Iatroscan responses for equal weights of squalene (SQ), methyl oleate (MO) and triolein (TO) on Chromarods-SII without exposure to iodine vapour (A), and after exposure to iodine vapour(B). O designates the point of application of sample; S and E refer to the start and end of the scans, respectively. For development solvent see text.

This process would retard the loss through premature vaporization of the more volatile material from the Chromarod prior to entering the flame proper and thus give an improved response.

Boiling points are not very meaningful in studying vaporization from thin or adsorbed films. For example the boiling points listed for squalene, methyl oleate and triolein are respectively 280, 218 and 235°C at pressures given[6] as 17, 20 and 18 mmHg. A more reliable comparison is the GLC retention time, and triolein would elute long after methyl oleate. For this reason the volatility of triolein may be taken as very low with or without added iodine. Its molecular weight of 885 is much higher than that of squalene (410) and methyl oleate (296). On an equal weight basis the squalene would have four ethylenic bonds to each one in methyl oleate (or triolein), hence the more dramatic response effect shown in Fig. 1 for squalene *versus* little or no increase for methyl oleate (the peak height on Fig. 1 is misleading, averaged areas were about the same for methyl oleate in sets A and B).

It is ironic that in the GLC of triglycerides the relative FID response decreases with increasing mass[7], although this is not a property of FID proper but of losses of triglycerides prior to FID.

It should be noted that moderate proportions of halogens do not affect FID

response[2]. Our observations show that other than the types of oxygen and sulphur heteroatoms present on carbon in a molecule, relative volatility also affects the FID response of the Iatroscan. Solvent focussing to produce narrower peaks also improves response for a given mass of material[5]. This also supports the concept of loss of material desorbed by heat prior to entering the flame. Some improvement to the design (geometry) of the Iatroscan detector appears desirable to enhance the response of the more volatile components.

Pending more thorough investigation of reproducibility, comparison of different halogens, and of a wider variety of unsaturated molecules, iodine vapour treatment of Chromarods is suggested as a means of improving sensitivity for volatile molecules with appropriate structures, probably including the nitrogenous bases. There is also potentially some scope for this treatment in classifying organic materials by type or extent of unsaturation.

ACKNOWLEDGEMENT

This work was supported by the Natural Sciences Research and Engineering Council of Canada.

REFERENCES

1 R. G. Ackman, *J. Gas Chromatogr.*, 2 (1964) 173.
2 R. G. Ackman, *J. Gas Chromatogr.*, 6 (1968) 497.
3 J. K. Kaitaranta and N. Nicolaides, *J. Chromatogr.*, 205 (1981) 339.
4 T. N. B. Kaimal and N. C. Shantha, *J. Chromatogr.*, 288 (1984) 177.
5 R. P. Delmas, C. C. Parrish and R. G. Ackman, *Anal. Chem.*, 56 (1984) 1272.
6 R. Weast (Editor), *Handbook of Chemistry and Physics*, CRC, Cleveland, OH, 51st ed., 1970, pp. C314, C398, C492.
7 R. J. Hamilton and R. G. Ackman, *J. Chromatogr. Sci.*, 13 (1975) 474.