Journal of Chromatography, 447 (1988) 230–233
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 560

Note

Determination of plasticizers in fat by gas chromatography–mass spectrometry

J. B. H. VAN LIEROP* and R. M. VAN VEEN
Food Inspection Service, Nijenoord 6, 3552 AS Utrecht (The Netherlands)
(First received January 21st, 1988; revised manuscript received March 28th, 1988)

Plasticizers, *e.g.*, phthalates, adipates and sebacates, used in food wrapping materials may migrate into the food. Limits have been placed on the presence of these compounds by the Packaging and Food Utensils Regulation of the Dutch Food Law[1]. Therefore analytical methods are required for their determination at the ppm level in foods. Capillary gas chromatography–mass spectroscopy (GC–MS) proved to be a very suitable means for quantifying the migration of plasticizers[2]. The clean-up procedure for the plasticizers in aqueous media is relatively simple. Separation of the plasticizers from fat however is rather difficult and time consuming. Techniques like thin-layer chromatography and liquid chromatography have been applied but often separation is not complete. Consequently, residual fat may damage the high-performance GC capillary columns.

The method now presented is based on the removal of the plasticizers from the fat by purging it with a flow of nitrogen at high temperature. In this way 1–10% of the plasticizers present in the fat are volatilized and subsequently trapped on the Tenax GC adsorbent. The hexane extract of the Tenax is suitable for GC–MS analysis. Fifteen plasticizers with boiling points higher than 240°C were determined in this way when added to a synthetic mixture of triglycerides (HB307). The method was also applied to a retail sample of liverwurst packed in a PVDC casing containing di-*n*-butyl sebacate and acetyl tri-*n*-butyl citrate as plasticizers.

EXPERIMENTAL

Materials

The following materials were used: Tenax GG adsorbent; antifoam solution on a silicone base; a synthetic mixture of triglycerides (HB 307); hexane and the plasticizers mentioned in Table I.

All utensils were extracted with hexane before use.

Preparation of test samples and internal standard

Suitable amounts of plasticizers were added to 10 ml of HB 307 usually in the 60 ppm range, because a global migration of 60 ppm is the limit according to Dutch Food Law. A solution of diisobutyl adipate, diisobutyl phthalate and di-2-ethylhexyl adipate in HB 307 containing such amounts was used as an internal standard.

0021-9673/88/$03.50

TABLE I

Plasticizer	*Formula*	*Molecular weight*	*Boiling point (°C)*	*Characteristic mass*	*Scan No.*
Dimethyl phthalate	$C_{10}H_{10}O_4$	194	282	163	282
Diethyl phthalate	$C_{12}H_{14}O_4$	222	296	149	327
Diisobutyl adipate	$C_{14}H_{26}O_4$	258	282	129	356
Diisobutyl phthalate	$C_{16}H_{22}O_4$	278	295	149	425
Di-*n*-butyl phthalate	$C_{16}H_{22}O_4$	278	340	149	430
Di-*n*-butyl sebacate	$C_{18}H_{34}O_4$	314	344	241	537
Acetyl tri-*n*-butyl citrate	$C_{20}H_{34}O_8$	402	378	129 185	572
Diethylhexyl adipate	$C_{22}H_{42}O_4$	370	–	129	626
Di-2-ethylhexyl phthalate	$C_{24}H_{38}O_4$	390	–	149	700
Di-*n*-octyl azelate	$C_{25}H_{48}O_4$	412	–	171	800

Determination of plasticizers in fat

A 10-ml portion of the fat was transferred to a three-necked vessel. The internal standard solution (1–60 ppm depending on the expected migration) in HB 307 and an antifoam solution were added. The vessel was connected to a Tenax absorption column and subsequently heated at 210°C in an oil-bath. The temperature of the contents of the vessel was about 180°C. While heating the vessel, nitrogen was passed through the fat at a rate of about 170 ml/min for 30 min. The Tenax (*ca.* 15 mg) was extracted with 1–3 ml hexane. This extract can be concentrated if high sensitivity is required. A 1-μl volume of this hexane extract was analyzed under the following GC–MS conditions.

The analyses were carried out by means of a Finnigan 4000 GS–MS system in the electron-impact mode and with a Finnigan 6115 data system. A 1-μl volume of the hexane extract was split injected on a 30 m × 0.32 mm I.D. DB 5 fused-silica column, operated with the following temperature programme: 3 min at 60°C, then to 300°C at 40°C/min, finally held at 300°C for 15 min. Helium was used as the carrier gas. The data system was tuned to the m/z values corresponding to the plasticizer in question.

Determination of plasticizers in fatty foods

For the determination of plasticizers in food, first the fat content of the food was determined. A sample of food was taken so as to obtain at least 10 ml fat. This sample was mixed with twice its weight of dry sodium sulphate. The mixture was extracted with diethyl ether in a Soxhlet apparatus for 6–7 h. The ether was removed by evaporation. The plasticizers in a portion of 10 ml of this fat obtained from the food were determined as described above.

RESULTS

The plasticizers determined by this method are recorded in Table I. Even the high boiling di-*n*-octyl azelate (DOAZ) could be detected by this method. Additions

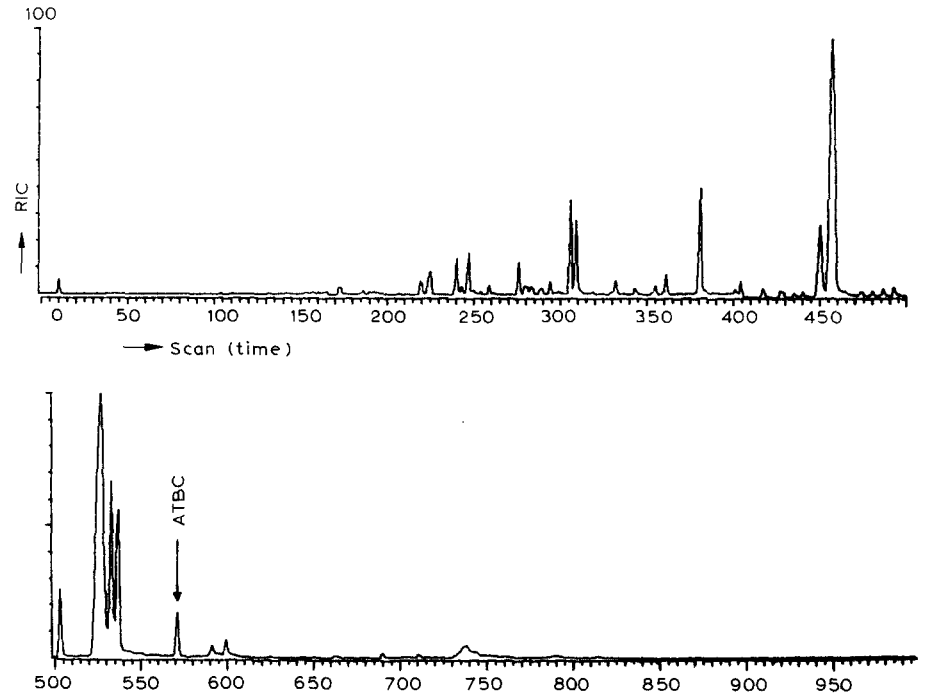

Fig. 1. Reconstructed ion chromatogram of liverwurst.

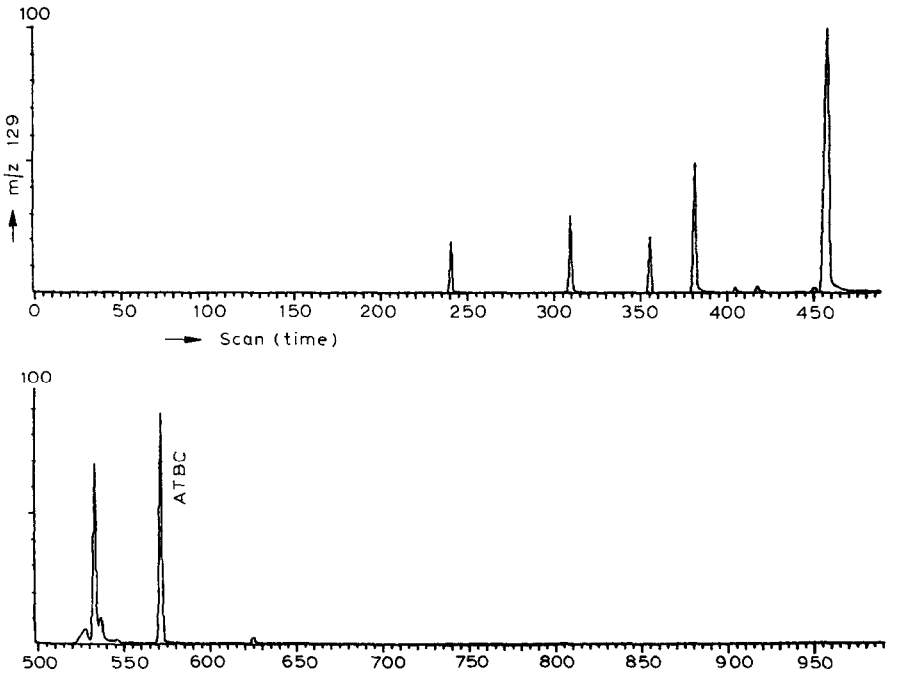

Fig. 2. Mass fragmentogram at m/z 129 for liverwurst showing the plasticizer acetyltri-*n*-butyl citrate.

of 1–10 ppm of the plasticizers to the fat could be detected. Fig. 1 shows a reconstructed ion chromatogram (RIC) pertaining to a retail sample of liverwurst. Fig. 2 shows a mass fragmentogram at m/z 129 used to detect acetyl tri-*n*-butylcitrate. The difference between these two chromatograms illustrates the power of multiple-ion detection (MID). The amounts of di-*n*-butyl sebacate and acetyl tri-*n*-butyl citrate migrated were about 30 mg/kg liverwurst.

DISCUSSION

The results obtained in this preliminary investigation indicate that it is possible to determine by means of GC–MS the migration of high-boiling plasticizers like phthalates and adipates from packaging materials into fatty foods in ppm quantities.

In spite of the low recovery (1–10% of the plasticizers), a sufficient amount of the plasticizers was obtained to carry out determinations at the required ppm level. The method is applicable to a wide range of compounds because the mass fragmentographic detection is specific. The lower limit of detection depends on the volatility and the presence of characteristic peaks in the mass spectrum of each plasticizer. An estimate of the detection limit of the method can be made as follows. Starting with 10 ml fat containing 10 ppm of a plasticizer and assuming that 1% of the plasticizer is trapped on the Tenax, the total amount in the hexane extract is 1 μg. If we evaporate this extract to 10–100 μl a concentration of 10–100 ng/μl is obtained, which can easily be detected by GC–MS. A large number of plasticizers together with suitable internal standards can be investigated in one determination. Quantitations can be carried out by the use of labelled compounds. Experiments with deuterated di-2-ethylhexyl phthalate as an internal standard for di-2-ethylhexyl phthalate are in progress.

REFERENCES

1 *Packaging and Food Utensils Regulation*, Staatsuitgeverij, 's-Gravenhage, 1980.
2 J. R. Startin, I. Parker, M. Sharman and J. Gilbert, *J. Chromatogr.*, 387 (1987) 509–514.