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SEPARATION OF PERMITTED AND NON-PERMITTED SOLVENTS FOR USE IN FOODSTUFFS BY GAS CHROMATOGRAPHY AND THE USE OF A SOLID SAMPLER FOR THE ESTIMATION OF RESIDUAL SOLVENTS IN OILS AND OLEORESINS

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SUMMARY

A simple method for the estimation of residual solvents in oils and oleoresins has been developed. This method incorporates the use of a solid sampler which enables only the volatile solvent to be added to the top of the gas chromatographic column, the residual oil being retained in the sample holder, thus preventing contamination of the stationary phase.

INTRODUCTION

Solvents are used in the food industry in two main ways: firstly for the extraction of oils and oleoresins, fixed or otherwise and in the decaffeination of coffee, where the solvent is subsequently removed; and secondly as carriers for food flavourings, vitamins, colorants, etc., where the solvent is essential to ensure adequate mixing of such substances into the foodstuff. The solvents concerned become ingredients of the foodstuff and are consumed; water and ethanol are commonly used. As from November 1969 the Solvents in Food Regulations 1967 (Statutory Instrument 1967, No. 1582) come into force. These regulations permit only ethanol, diethyl ether, ethyl acetate, glycerol and its mono-, di- and tri-acetates, propan-2-ol and propane-1,2-diol to be used as solvents in foodstuffs, where the solvent will form an ingredient of the foodstuff and be consumed as such.

Most of the work published on the detection of solvent residues in foodstuffs has been done on the estimation of traces remaining in solvent-extracted meals, oils and oleoresins. Direct extraction with a suitable solvent and gas chromatographic examination of the extract have been used[1,2]. Gas chromatographic examination of the headspace of oleoresins under suitable conditions has also been employed[3]. The most widely used method where applicable is steam distillation and extraction of the distillate with a suitable extractant and examination of this by gas chromatography[4,5]. In the case of residual solvent in oils direct injection of the oils into the gas chromato-

graph has been used[6] but the problem of column contamination greatly restricts this method. Steam distillation and extraction are lengthy techniques with risk of losses and a quicker method has been sought for the detection of low boiling solvents in oils, oleoresins and other foodstuffs.

Recently the use of solid samplers in gas chromatography has found wide applications in many fields. The main advantage is that there is no masking by a large diluent peak of trace components in a sample. The injection of sintered glass pellets on which the sample has been evaporated has been used for injecting volatile fatty acids[7]. Automatic continuous systems of solid sample injections have been used for the introduction of steroids in small ferrous metal capsules which are subsequently removed from the top of the columns by a solenoid-activated electromagnetic field[8]. Similar systems have been employed using stainless steel gauzes onto which samples have been evaporated and which are dropped from a rotating wheel at appropriate intervals onto the top of a heated column[9]. Encapsulation of samples in polythene or indium capsules which are subsequently melted with the release of volatiles from the sample have been used successfully[10,11]. The use of modified syringes where the sample is held in a needle for a short time and withdrawn through a valve if necessary has been described[12–14]. Sealing of a sample in a glass capillary which is subsequently crushed on top of the gas chromatographic column has also been reported to give reproducible results[15,16]. A solid sampler of this latter type was thought to be most suitable for use in the food field. However, the removal of the crushed capillary and contents following release of the volatiles without interruption of the gas flow

TABLE I

POSSIBLE SOLVENT RESIDUES IN FOOD PRODUCE

	Boiling point
Permitted solvents	
Ethyl acetate	77.2
Ethyl alcohol	78.5
Glycerol	290.0
Glycerol monoacetate	158.0
Glycerol diacetate	280.0
Glycerol triacetate	259.0
Monopropylene glycol	189.0
Propan-2-ol	82.3
Other solvents likely to be used	
Amyl acetate	142.0
Benzyl alcohol	205.0
Butane-1,3-diol	204.0
Butyl acetate	124.0
Diethyl tartrate	280.0
Ethyldigol	202.0
Hexane	68.7
Isopropyl myristate	192.6/20 mm Hg
Methanol	64.7
2-Methoxyethanol	124.0
2-Methylpentane-2,4-diol	206.5
Propan-1-ol	97.2
Triethyl citrate	294.0

TABLE II

RETENTION TIMES OF A VARIETY OF SOLVENTS, INCLUDING THOSE PERMITTED IN FOOD, ON AN ANTAROX CHROMATOGRAPHIC COLUMN

Injection volume: 1 μl of solution in methanol.

Temperature (°C)	*Solvent*	*Retention time* (*min*)
150	Ethyldigol	1.7
	Propane-1,2-diol	1.5
	Butane-1,3-diol	2.7
	2-Methylpentane-2,4-diol	1.7
	Benzyl alcohol	4.7
	Isopropyl myristate	10.6
168	2 Methylpentane-2,4-diol	0.9
	Butane-1,3-diol	1.5
	Benzyl alcohol	2.5
	Isopropyl myristate	5.2
	Glycerol triacetate	5.2
190	Butane-1,3-diol	0.7
	Isopropyl myristate	2.3
	Benzyl alcohol	1.2
	Glycerol triacetate	2.3
	Glycerol diacetate	2.4
	Glycerol monoacetate	4.0
	Diethyl tartrate	7.2
	Triethyl citrate	8.8

would be necessary to prevent contamination of the column by higher boiling components. Such an application has now been developed in this laboratory.

The work discussed in this paper describes the gas chromatographic separation of a wide range of solvents of a type used in food manufacture and the development of a solid sampler in which the sample is sealed in a glass capillary. This sampler has been used to estimate the more volatile solvents; hexane and trichloroethylene in fixed oils and oleoresins have been quantitatively determined.

EXPERIMENTAL

Chromatographic separation of solvent residues

Several stationary phases have been reported in the literature for use in the separation, identification and estimation by gas–liquid chromatography of solvent mixtures. RAWLINSON AND DEELEY[17] used a stationary phase consisting of 8% butane-1,4-diol succinate on hexamethyldisilazane-treated Chromosorb W (80–100 mesh) for the separation of high-boiling esters. WATTS AND HOLSWADE[6] used 10% didodecyl phthalate on Chromosorb P (60–80 mesh) for the separation of hydrocarbon solvents and there are reports on the use of 25% Apiezon L on Celite (60–80 mesh) for the separation of a variety of residual solvents. The solvents used at present and those likely to be used in the future are listed in Table I. This shows that the range of boiling points of these solvents may vary from 50° to 320°. It is therefore likely that more than one type of column will be required in the separation of the variety of possible solvent residues. Many stationary phases were investigated and Tables II

TABLE III

RETENTION TIMES OF A VARIETY OF SOLVENTS, INCLUDING THOSE PERMITTED IN FOOD, ON A PORAPAK S CHROMATOGRAPHIC COLUMN

Injection volume: 1 μl of solution in methanol.

Temperature (°C)	*Solvent*	*Retention time* (*min*)
150	Methanol	1.7
	Ethanol	2.7
	Ethyl acetate	9.0
	Propan-2-ol	4.7
	Propan-1-ol	6.7
	Hexane	10.6
200	Methanol	1.3
	Propan-2-ol	1.7
	Amyl acetate	13.3
	Propan-1,2-diol	5.6
	Butane-1,3-diol	18.6
	2-Methylpentane-2,4-diol	28.6
	Ethyldigol	37.0
	2-Methoxyethanol	3.7
	Benzyl alcohol	38.5
	Glycerol	40.0
220	Glycerol monoacetate	39.0
	2-Methylpentane-2,4-diol	12.4
	Benzyl alcohol	16.0
	Ethyldigol	14.6
	Butane-1,3-diol	8.3
	Amyl acetate	8.9
	Butyl acetate	5.7

and III give the retention times of a number of solvents on the two most successful columns. Table II shows the retention time for a mixture of solvents, using an Antarox column consisting of 8 % Antarox CO-990 absorbed on AW-DMCS Chromosorb W (80–100 mesh) and Table III gives retention times using a Porapak S column (100–120 mesh). Two other stationary phases were also used with some success. A column of 5 % FFAP (free fatty acid phase) on AW-DMCS Chromosorb G (80–100 mesh) acted very similarly to the Antarox column but the use of 25% Apiezon L on Celite (60–80 mesh) gave too long retention times and accurate estimation of trace quantities was not possible. All the columns used were 185 cm long and had an external diameter of 3 mm. Standard solutions of all the solvents were prepared at the 10 p.p.m. level in methanol and 1 μl samples were injected onto the top of the column. A Philips PV 4000 chromatograph was used for this work. The Antarox column was very successful in the separation and determination of most of the higher boiling solvents but in the case of solvents with boiling points of $< 100°$ the eluting peaks became involved with the tail from the methanol. However, the Porapak S column gave excellent separation of the low boiling esters, hydrocarbons and alcohols.

Solvent residues in edible oils

The problem of solvent residues in edible oils exists for all solvent-extracted edible oils which are then refined for human consumption. In the case of olive oil or

castor oil three solvents have been generally used in the past for extraction. These are hexane, trichloroethylene and carbon disulphide. Of these, the latter is now no longer used and the most popular extraction solvent is hexane, trichloroethylene being used to a very limited extent. It is probable that in "residue olive oil", *i.e.* oil extracted from the pressed pulp of the olive, and "which has undergone a complete refining process including deodorization ("stripping") at a temperature which is more than twice as high as the solvent's distillation temperature, no trace of solvent should be found". However, the present method of analysis, that of direct injection onto the top of the column, is not at all satisfactory as it rapidly changes the character of the stationary phase and greatly affects the sensitivity of the detection system. The use of a solid sampler (Fig. 1), however, gets over the problem as only the volatiles are injected onto the top of the column and continuous injection of samples for several weeks has little or no effect on the stationary phase.

Method

The solid sampler (Fig. 1) is connected to a gas chromatographic system con-

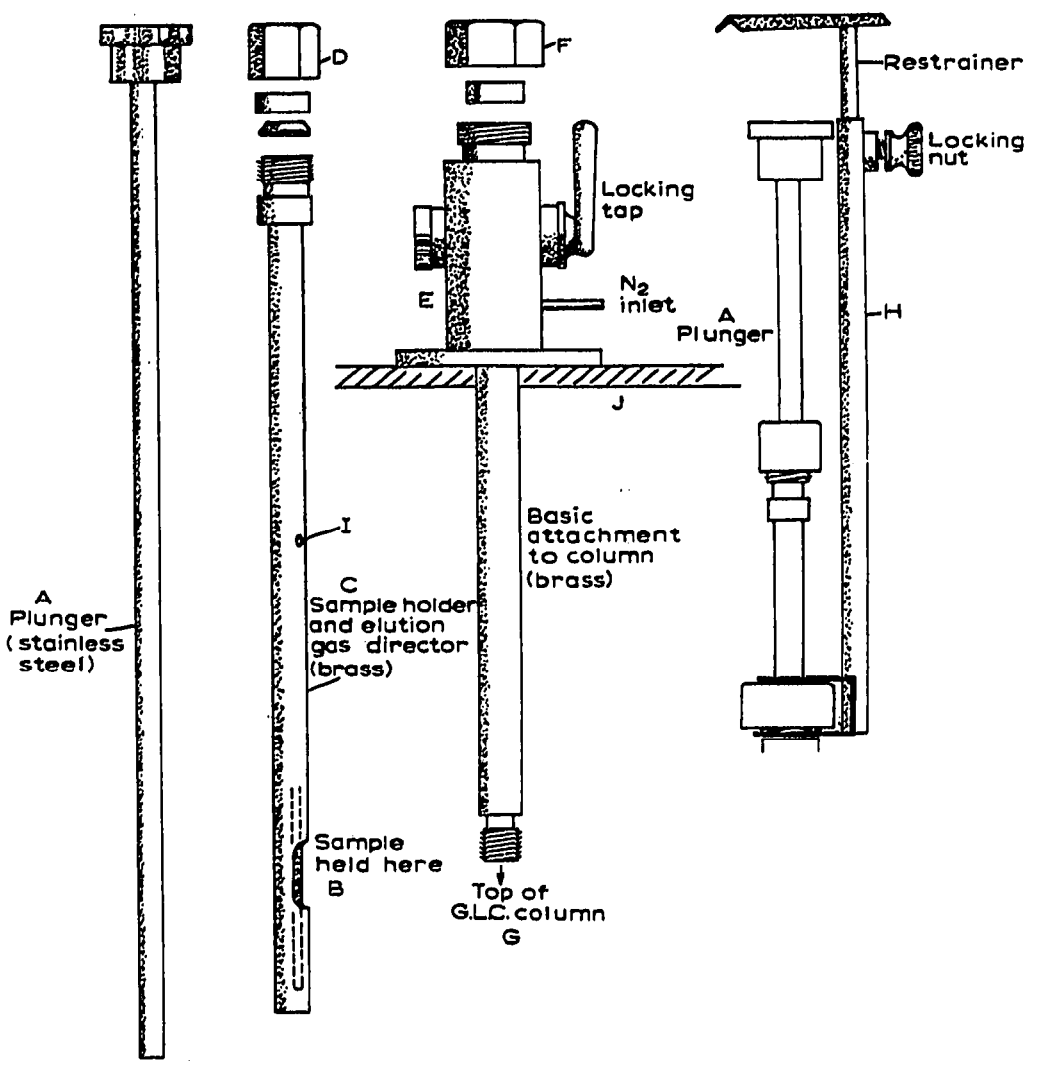

Fig. 1. Gas–liquid chromatography solid sampler.

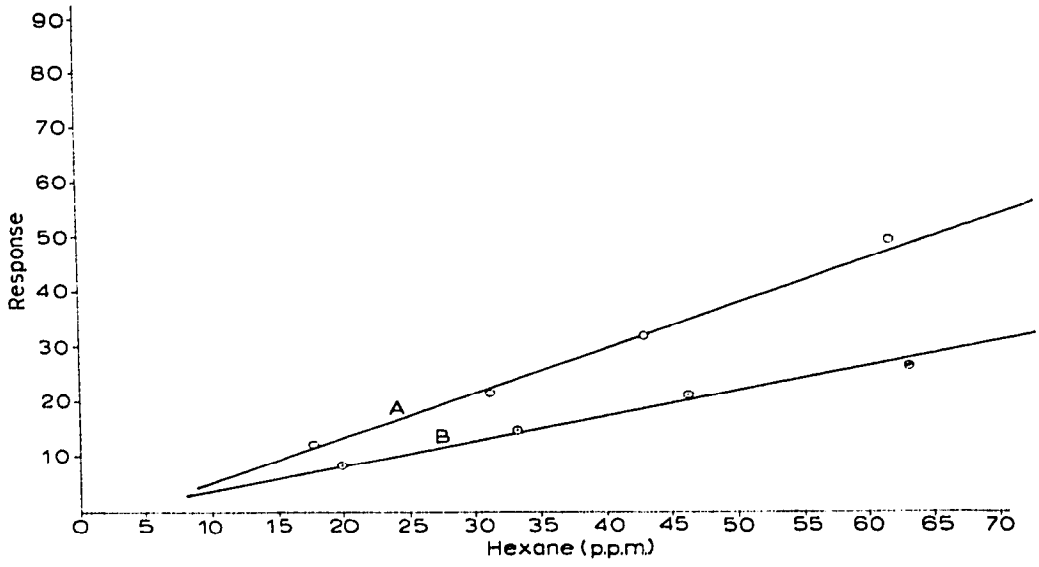

Fig. 2. Response of the flame-ionisation detector to hexane and trichloroethylene in olive oil. A = hexane in olive oil; B = trichloroethylene in olive oil.

sisting of a 185-cm Porapak S (100–120 mesh) column of 3 mm O.D. operated at 200°. Hexane and trichloroethylene residues are estimated in olive oil and castor oil.

The method of handling the sample is determined by its viscosity. Olive oil is injected into a capillary tube 12.5 mm long and sealed at one end, using a 10 μl microsyringe. Castor oil is transferred to the capillary using an Agla syringe. The tube is sealed at the other end and placed in compartment B of the solid sampler (Fig. 1). The plunger A is inserted into the top of the cylinder C and an airtight seal is made by fastening nut D. The assembled cylinder and plunger are then inserted in the outer cylinder E, and an airtight seal is made by fastening nut F. The outer cylinder E passes through the top of the oven J of the chromatograph and is connected to the chromatographic column G. With the carrier gas supply switched on and restrainer H in position to prevent ejection of the plunger, the sample is left in compartment B for 3 min to reach equilibrium. The plunger is then depressed until the glass capillary

TABLE IV

RECOVERY OF *n*-HEXANE AND TRICHLOROETHYLENE FROM OLIVE OIL

Solvent	*Added (p.p.m.)*	*Recovered (p.p.m.)*	*Retention time (min)*	*Recovery (%)*
Hexane	5	4.5	2.6	90
	10	9.1	2.6	91
	20	18.2	2.6	91
	50	49.1	2.6	98
	100	99	2.6	99
Trichloroethylene	5	4.7	4.0	95
	10	9.8	4.0	98
	50	50	4.0	100
	100	100	4.0	100

is broken and then raised again until the bottom of the plunger is just above the level of the vapour outlets I. This allows the volatile vapours from the sample to pass through I down onto the column. The plunger is kept in position by adjustment of restrainer H. The components in the sample are detected using a flame-ionisation detector. When the analysis is complete, F is loosened and C and A are removed together and the remaining glass and oil held in B are removed and the next sample is placed in position.

Fig. 2 shows the response of the flame-ionisation detector to olive oil samples containing standard hexane and trichloroethylene residues and Table IV shows the recoveries obtained for hexane and trichloroethylene for various concentrations of these solvents in olive oil. Traces down to 5 p.p.m. (of these solvents in oils) can be estimated and continuous injection over a number of weeks does not affect the column or the retention time of the solvents.

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