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DETERMINATION OF PHENOLIC PLASTIC ADDITIVES IN EDIBLE OILS BY THIN-LAYER CHROMATOGRAPHY

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SUMMARY

An analytical method has been developed for the determination of five sterically hindered phenolic plastic additives in different edible oils. The procedure is based on thin-layer chromatography (TLC), after extraction of the additives from the matrix. The co-extracted oil components are eliminated by the use of pre-treated-silica plates. The additives are revealed according to the procedure developed by Boute and determined quantitatively by a monochromator TLC scanner. The detectable concentration of the individual antioxidants, in 5 g of the oil, ranges from 50 ppb* to 2 ppm, depending on the nature of the additive and the oil. The validity of the proposed method is based on investigations using sesame oil, safflower oil, sunflower oil, corn-germ oil and olive oil.

INTRODUCTION

The plastic packaging of foodstuffs has proven to be most suitable in conservation processes. However, the quality of the packed product may change as a result of the migration of plastic components into the food. In order to understand and control such migration mechanisms, it is necessary to develop accurate and simple methods for the detection of these contaminants in the complex food matrix. Most of the earlier work has been concentrated on the identification of food preservatives[1–6].

The aim of this paper is the analyses of traces of some plastic additives in edible oils. The choice of both the phenolic antioxidants and the oils has to be related to important parameters of the migration mechanism, namely the size of the migrant and the composition of the foodstuff[7,8]. Earlier attempts to apply luminescence spectroscopy to achieve the identification of commercial plastic additives[9] in food simulants, including work in our laboratory[10], met with little success when applied to edible oils.

The selected plastic additives are: 1,6-hexanediol bis-[3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)propionate]; pentaerythrityl tetrakis-[3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)propionate]; octadecyl 3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)propionate; N,N'-hexamethylenebis-(3,5-di-*tert.*-butyl-4-hydroxyhydrocinnamamide); 1,3,5-trimethyl-2,4,6-tris-(3,5-di-*tert.*-butyl-4-hydroxybenzyl) benzene, subsequently referred to as antioxidant I, II, III, IV and V, respectively (see Table I).

* Throughout this article, the American billion (10^9) is meant.

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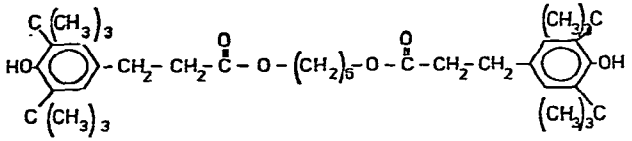
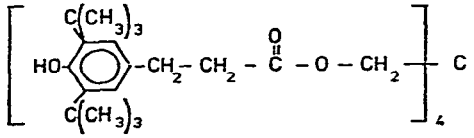
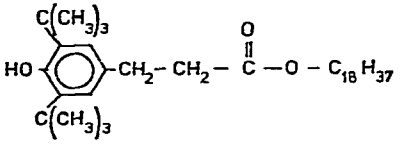
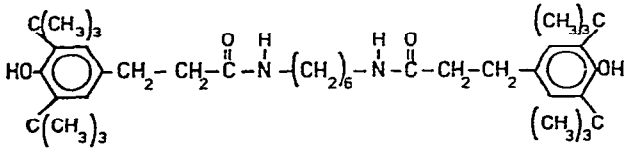
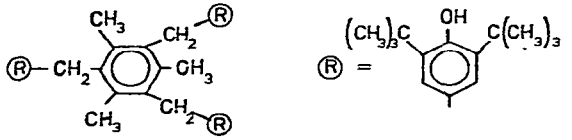
TABLE I

CHEMICAL STRUCTURES OF THE FIVE ANTIOXIDANTS AND THE SOLVENTS USED FOR EXTRACTION

Antioxidant	*Chemical structure*	*Extractant*
I		Acetonitrile
II		Acetonitrile
III		Dimethylformamide
IV		Methanol
V		Dimethylformamide

EXPERIMENTAL

The thin-layer chromatography (TLC) apparatus comprised an automatic injector and a TLC scanner with monochromator (Camag, Muttenz, Switzerland). The TLC plates used were precoated with SiO_2 HR 25-UV 254 (Machery, Nagel & Co., Düren, G.F.R.). Antioxidants I, II, III, IV and V were obtained from Ciba–Geigy (Basle, Switzerland) and Shell (Amsterdam, The Netherlands), thioglycol acid 2-ethylhexyl ester ("RSH") and the unrefined edible oils were respectively purchased from Fluka (Buchs, Switzerland) and general commercial sources.

Stock solutions of the five antioxidants in chloroform were added to the edible oils. The chloroform was evaporated, and the oils (spiked with the additive) were used for extraction and recovery measurements. Aliquots of the stock solutions and oil extracts were spotted on a TLC plate and treated as described under *Procedures*. The peak area of the reference spot was integrated with a computing integrator (Techmation 306), and the calibration graph was constructed by plotting the peak area (arbitrary counts) of each antioxidant against the concentration. A linear

detector response for each substance was obtained by establishing an absolute calibration curve for sample volumes ranging from 1–25 μl.

Procedures

(A). For the extraction of antioxidants I and II from the different oils, 5 g of the oil was diluted with 20 ml of 2-methylbutane [containing 100 ppm of butylated hydroxytoluene (BHT) and 250 μl of RSH] and extracted with a total volume of 20 ml of acetonitrile (5 ml per extraction). The acetonitrile extract was washed with 5 ml of 2-methylbutane and evaporated to dryness on a rotary evaporator; the residue was dissolved in 1 ml of chloroform. Aliquots of this solution were spotted on a TLC plate that had been sprayed (8 cm) with aqueous 10% $AgNO_3$ solution and dried at 120°C for 5 min. The plate was developed in benzene–chloroform (95:5). After evaporation of the residual solvent and revelation of the antioxidants by the Boute reaction[11], the yellow spot of the nitroso-derivative was scanned at 405 nm for antioxidant II and 436 nm for antioxidant I.

(B). Antioxidants III and V were extracted from the oil by four successive 5-ml portions of dimethylformamide. The extract was diluted with 200 ml of 5% (v/v) aqueous phosphoric acid and then extracted with a total of 60 ml of benzene in four extractions. After evaporation of the benzene, the residue was dissolved in chloroform, and aliquots were spotted on a 3-cm $AgNO_3$-impregnated TLC plate; the plate was developed successively with benzene–chloroform (90:10) and with trichloroethylene over a distance of 5 and 15 cm, respectively. The spot was revealed as described in (A) above.

(C). The extraction of antioxidant IV from 5 g of oil, diluted with 20 ml of *n*-heptane (8% of RSH), was incomplete with four successive extractions with 5 ml of methanol. After evaporation of the solvent, the residue was dissolved in chloroform, and aliquots were spotted on a TLC plate (with a concentration zone), which was developed with dichloromethane–diethyl ether (60:40); spots were visualised by using the Boute reaction and measured at 436 nm.

RESULTS AND DISCUSSION

Extraction

The direct identification of small quantities of antioxidants in edible oils was not feasible, owing to interference by other materials in the oil. The antioxidants were therefore extracted from the matrix prior to identification procedures. Good recoveries of antioxidants I, II and IV were achieved if the initial oil sample was diluted with a non-polar solvent that was not miscible with the extractant. Also, the addition of RSH increased the recovery by a factor of almost 2. The extraction of antioxidant III from safflower and sesame oil was very poor.

Thin-layer chromatography

In order to reveal the antioxidants on the TLC plate, a very sensitive spray reagent was used. Phenolic substances form nitroso derivatives according to a reaction described by Boute[11]. The high sensitivity of this colour reaction (related to the number of phenolic groups on each molecule) makes it possible to detect trace amounts of the five antioxidants. Table II summarises the detection limit of each

TABLE II

DETECTION LIMITS AND RECOVERY OF FIVE ANTIOXIDANTS IN DIFFERENT EDIBLE OILS BY THIN-LAYER CHROMATOGRAPHY

Antioxidant	*Oil*	Q_{max}* *(µl)*	*DL*** *(ng)*	*DA**** *(ppb)*	*Recovery§ (%)*	
					Without RSH	*With RSH*
I	Olive oil	80	30	125	45	79.9
	Safflower oil	80	50	125	55	86.1
	Sesame oil	25	50	400	45	65.5
	Sunflower oil	80	50	125	—	77.7
	Corn-germ oil	25	50	400	—	75.2
II	Olive oil	80	20	50	36	68.4
	Safflower oil	80	20	50	35.5	74.1
	Sesame oil	25	20	150	32.2	77.7
	Sunflower oil	80	20	50	—	85.9
	Corn-germ oil	25	20	160	—	78.1
III	Olive oil	25	50	800	97	
	Safflower oil	15	50	1.400	25	
	Sesame oil	15	50	1.400	33	
	Sunflower oil	15	50	1.600	61	
	Corn-germ oil	10	50	2.500	70	
IV	Olive oil	5	50	2.000		40
	Safflower oil	5	50	2.300		30
	Sesame oil	5	80	2.500		35
	Sunflower oil	5	50	2.000		30
	Corn-germ oil	5	50	2.000		40
V	Olive oil	25	5	80	83.6	
	Safflower oil	15	5	140	82.6	
	Sesame oil	15	5	140	67.8	
	Sunflower oil	15	5	140	68.3	
	Corn-germ oil	10	5	250	93.4	

* Volume applied to the plate.
** Detection limit on the plate.
*** Detectable amount of antioxidant in the oil.
§ Recovery percentage after extraction.

antioxidant in different oils, the recovery data of the oil extraction and the amount of each substance detectable in the oil.

CONCLUSION

A procedure has been devised for the routine analysis of some plastic migrants in edible oils. The selected sterically hindered phenols, which can migrate from the packaging plastic into the contacting oils, will only be present in trace amounts. Before quantification of the different migrants, pre-concentration of the additives has to be carried out (*e.g.*, extraction). The phenolic antioxidants are successfully separated from the co-extracted oil, and from interfering oil components, by TLC on $AgNO_3$-impregnated SiO_2 layers. After development, the antioxidants are identified by the formation of a nitroso derivative[11]. The detection limit for each antioxidant on the

TLC plate is between 5 and 80 ng, depending on the chemical structure of the substances. The combination of extraction and TLC makes it possible to detect 200 ppb of antioxidants I, II, and V in some edible oils.

The scope of the method could be extended to a wide variety of fatty food products, provided that the extraction step was sufficiently selective. For analysis purposes, TLC has a great potential in the identification of plastic additives, particularly phenolic antioxidants, which migrate into fatty foods.

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