

Production Process Contamination of Citrus Essential Oils by Plastic Materials

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Twelve samples of plastic materials employed in the industrial extraction of citrus essential oils were analyzed for the presence of phosphorated plasticizers, chloroparaffins, and phthalate esters. The samples tested were found to release these contaminants into the essential oils during the production process. Contamination tests were carried out using dichloromethane and uncontaminated samples of citrus essential oils as extractants. The extracts were analyzed by HRGC/FPD, ECD, and MS. Only one sample of plastic material was found to release triaryl phosphates, 5 samples released chloroparaffins, 6 released diisobutyl phthalate, and 8 released bis(2-ethylhexyl) phthalate. Significantly larger quantities of contaminants were released by new plastic parts than by used plastic parts.

Keywords: Plasticizers; essential oils; HRGC/FPD, ECD, MS

INTRODUCTION

In earlier studies we determined the levels of phosphorated plasticizer, phthalate ester, and chloroparaffin residues in citrus essential oils by gas chromatography with flame photometric (FPD), electron-capture (ECD), and mass-spectrometer (MS) detectors, and we concluded that the contamination was probably due to the use of plastic materials during the industrial extraction process (1–5).

We have now, therefore, turned our attention to the plastic components with which the essential oils come into contact during the industrial production cycle.

MATERIALS AND METHODS

Sampling. Samples of the subject plastic materials were obtained from the factories of Sicilian and Calabrian producers of citrus essential oils. The various plastic components analyzed, both new and used, are reported in Tables 1 and 2. Weighed amounts of these materials were left to stand in dichloromethane (1 g/10 mL) for 5 min at room temperature in an Erlenmeyer flask with a Teflon-lined screw cap. The same procedure was then repeated using uncontaminated essential oils as extractants. For every plastic sample tested, an aliquot of the dichloromethane and essential oil extracts was concentrated to dryness and analyzed by HRGC as described below.

Phosphorated Plasticizer Residues. Standards. Phosphorated plasticizer standards were purchased from Carlo Erba (Milano). A 1 ppm standard solution was prepared in *n*-hexane. As previously reported (2), the standard was composed of seven different triaryl phosphates (TAPs): triphenyl phosphate (TFP), diphenyltolyl phosphates (DFTF), phenyldi-tolyl phosphates (FDTF), tritolyl phosphates (TTF), ditolylxylyl phosphates (DTXF), tolyldixylyl phosphates (TDXF), and trixylyl phosphates (TXF) (Figure 1).

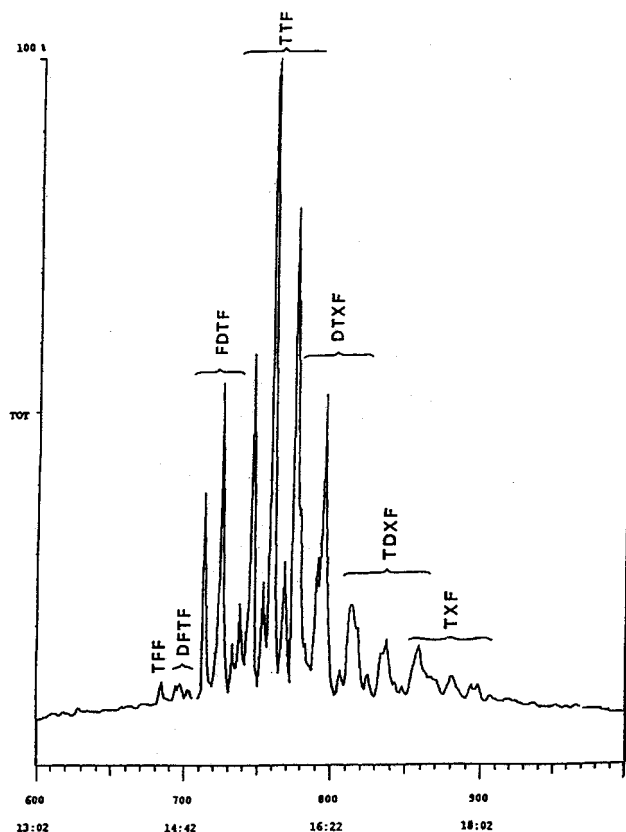


Figure 1. GC-MS chromatogram of the triaryl phosphate standard.

GC Analysis. Extracts were directly analyzed without cleanup procedures using a FPD-DANI 86.10 gas chromatograph, equipped with a MEGA 68 fused-silica capillary column (25 m × 0.32 mm i.d., 0.45 μm film thickness). The injector programmable temperature vaporizer (PTV) went from 65 to 240 °C at a rate of 999 °C/min and then was held for 4 min. The oven temperature program was 75 °C (5 min hold), increased to 100 °C at 7.5 °C/min, then to 170 °C at 2 °C/min

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Table 1. Levels of Contaminants Extracted from Plastic Components by Dichloromethane (Standard Deviation σ_{n-1} on the Mean of $n = 10$ Analyses)^a

component	condition	TAP's	CP	Di-iBuP	Bis2EtExP
A type 1	new	69 ± 5.4 ppm		0.3 ± 0.05%	3.2 ± 0.7%
A type 1	used				
A type 2	new				3.2 ± 0.9%
A type 2	used				105 ± 7.4 ppm
B type 1	new		5.5 ± 1.1%	1.6 ± 0.2%	
B type 1	used				
B type 2	new		8.9 ± 1.8%	2.1 ± 0.6%	0.6 ± 0.08%
B type 2	used		4.7 ± 0.8%	0.7 ± 0.2%	0.1 ± 0.02%
B type 3	new		1.5 ± 0.4%	2.4 ± 0.6%	0.8 ± 0.04%
C	new		15.7 ± 2.6%	3.8 ± 0.9%	0.5 ± 0.03%
C	used				
pump gasket	used				0.3 ± 0.04%

^a A = conveyor for fruits transport; B = tube for pouring and blending; C = tube for recycling emulsion; TAPs = triaryl phosphates; CP = chloroparaffins; Di-iBuP = diisobutyl phthalate; Bis2EtExP = bis-(2-ethylhexyl) phthalate.

Table 2. Levels of Contaminants Extracted from Plastic Components by Contact with Citrus Essential Oils (Standard Deviation σ_{n-1} on the Mean of $n = 10$ Analyses)

component	condition	TAP's	CP	Di-iBuP	Bis2EtExP
A type 1	new	6.3 ± 0.9 ppm		56 ± 5.4 ppm	280 ± 25 ppm
A type 1	used				
A type 2	new				520 ± 39 ppm
A type 2	used				7.2 ± 08 ppm
B type 1	new		320 ± 23 ppm	450 ± 52 ppm	
B type 1	used				
B type 2	new		340 ± 45 ppm	490 ± 28 ppm	150 ± 32 ppm
B type 2	used		290 ± 18 ppm	370 ± 17 ppm	22 ± 1.6 ppm
B type 3	new		210 ± 26 ppm	430 ± 36 ppm	240 ± 13 ppm
C	new		280 ± 31 ppm	490 ± 27 ppm	220 ± 16 ppm
C	used				
pump gasket	used				190 ± 33 ppm

^a For abbreviations A, B, C, TAPs, CP, Di-iBuP, and Bis2EtExP see Table 1.

(5 min hold), and finally to 250 °C at 10 °C/min. Helium was used as the carrier gas at a flow rate of 2 mL/min (split 6 mL/min). Quantitative analysis was based on the sum of all the areas, using bromophos-methyl as an internal standard. Under these conditions a detection limit of 0.01 ppm of total triaryl phosphates can be reached.

Chloroparaffin Residues. *Standards.* Chloroparaffin standards (CP) from C₆ to C₁₈ were purchased from Witco Corporation (Houston, TX). A 5 ppm standard solution was prepared in *n*-hexane. Silica gel (70–230 mesh) was obtained from Merck (Darmstadt) and dichloromethane was from Baker (Deventer; Holland).

Cleanup Procedure. A 10 mm i.d. × 500 mm length glass column with a Teflon stopcock was used. Silica gel was activated at 550 °C for 3 h. The chromatographic column was packed with a slurry of silica gel (8 g) in dichloromethane and the excess solvent was drained off (6–8). Aliquots (0.2 mL) of the dichloromethane extract solutions of each plastic material sample were introduced into the column and then eluted with 30 mL of dichloromethane. The first fraction (0–12 mL) was discarded and the second fraction (12–30 mL) was collected. This fraction was then concentrated under a gentle stream of nitrogen and analyzed by gas chromatography. The same procedure was repeated using aliquots of the essential oil extract solutions.

GC Analysis. The levels of chlorinated paraffins were determined with a Shimadzu GC-17A gas chromatograph with an electron capture detector and a Restek RTX-5 (30 m × 0.32 mm, 0.25 μm film thickness) column operating in the splitless mode. The injector temperature was maintained at 230 °C. The column oven temperature program was 50 °C (2 min hold) to 150 °C at a rate of 25 °C/min, then to 270 °C at 4 °C/min (20 min hold). Helium was used as the carrier gas at a constant flow linear rate of 36 cm/s. Quantitative analysis of total chloroparaffin levels was carried out by direct calibration, using the above-mentioned standard mixture. The height of the peak following the highest one of the chromatogram was taken into account. Because of the large number of isomers,

Table 3. Time Intervals, Selected Ion Monitoring, and Detection Limits for Phthalate Esters under Analysis

phthalate (P)	time (min)	SIM (<i>m/e</i>)	detection limit (pg)
DiMetP	6.5–8	163, 194	40
DiEtP	8–9.4	149, 177	10
DiPrP	9.4–10.2	149, 191, 209	8
Di-iBuP	10.2–10.9	149, 167, 223	3
DinButP	10.9–13	149, 223	4
ButBenP	13–14.2	149, 206	30
Bis2EtHexP	14.2–17	149, 167	6
DinOcP	14.42–17	149, 167	20

which give the chromatogram a characteristic appearance, the detection limit was estimated to be 1 ppm based on the sum of all the isomers present.

Phthalate Residues. *Standards.* Dimethyl phthalate (DiMetP), diethyl phthalate (DiEtP), dipropyl phthalate (DiPrP), diisobutyl phthalate (Di-iBuP), di-*n*-butyl phthalate (DinButP), butylbenzyl phthalate (ButBenP), bis(2-ethylhexyl) phthalate (Bis2EtHexP), and di-*n*-octyl phthalate (DinOcP), (99% purity) were purchased from Aldrich Chemical Co. (Milwaukee, WI). A solution containing a mixture of all the phthalates (1 μg/mL of each) was prepared in *n*-hexane.

GC Analysis. Extracts were directly analyzed without cleanup procedures using a Finnigan MAT GCQ gas chromatograph–mass spectrometer, equipped with a DB-5 MS fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The injector temperature was maintained at 250 °C. The transfer line was heated to 275 °C. The oven temperature program was from 60 °C to 275 °C at a rate of 15 °C/min and then held for 14 min. Mass spectra were recorded in the electron impact (EI) mode at 70 eV: full scan range 40–500 D; selected ion monitoring (SIM) was according to Table 3. Helium was the carrier gas at a flow rate of 40 cm/s. The injection volume was 1 μL. Quantitative analysis was carried out by comparing the peak areas with those of the standard mixture.

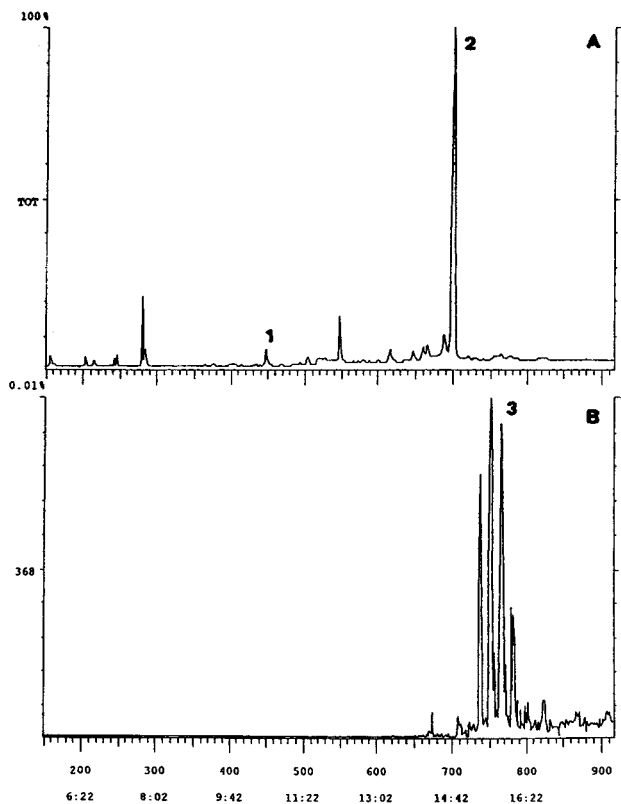


Figure 2. GC-MS chromatogram of CH_2Cl_2 extract "A type 1 (new)". A: total ion current; B: peaks at m/e 368: (1) diisobutyl phthalate; (2) bis(2-ethylhexyl) phthalate; (3) tritoly phosphates.

RESULTS AND DISCUSSION

The results reported in Table 1 show the mean levels (\pm SD) of contaminants extracted by dichloromethane, as calculated from 10 independent analyses.

A triaryl phosphates (TAPs) level of 69 ppm was found for the plastic component designated A Type 1 (new), but no other parts showed triaryl phosphate levels above the detection limit. The GC-MS chromatogram of A Type 1 (new) shows (Figure 2) the presence of diisobutyl phthalate and bis(2-ethylhexyl) phthalate in the total ion current (TIC), together with peaks at m/e 368, characteristic of the tritoly phosphates.

The B Type 1 (new) and C (new) extracts contained 5.5% and 15.7% of chloroparaffins (CP) respectively, but the corresponding used parts did not release any detectable level of these compounds. The B Type 2 extract released a quantity equivalent to 8.9% weight of chloroparaffins when new and 4.7% when used. Chloroparaffins (1.5%) were found in the B Type 3 (new) extract. The presence of diisobutyl phthalate and chloroparaffins can be seen in the GC-MS chromatogram of the B Type 1 (new) extract shown in Figure 3.

A similar trend was observed for phthalate ester residues in the dichloromethane extracts.

The diisobutyl phthalate (Di-iBuP) residues were: 0.3% weight in the A Type 1 (new) extract and undetectable in the extract from the corresponding used part; 1.6% in B Type 1 (new) and undetectable in the corresponding used part; 2.1% in B Type 2 (new) and 0.7% in the corresponding used part; 2.4% in B Type 3 (new); and 3.8% in C (new) and undetectable in the corresponding used part.

The bis(2-ethylhexyl) phthalate (Bis2EthexP) residues were: 3.2% in the A Type 1 (new) extract and undetect-

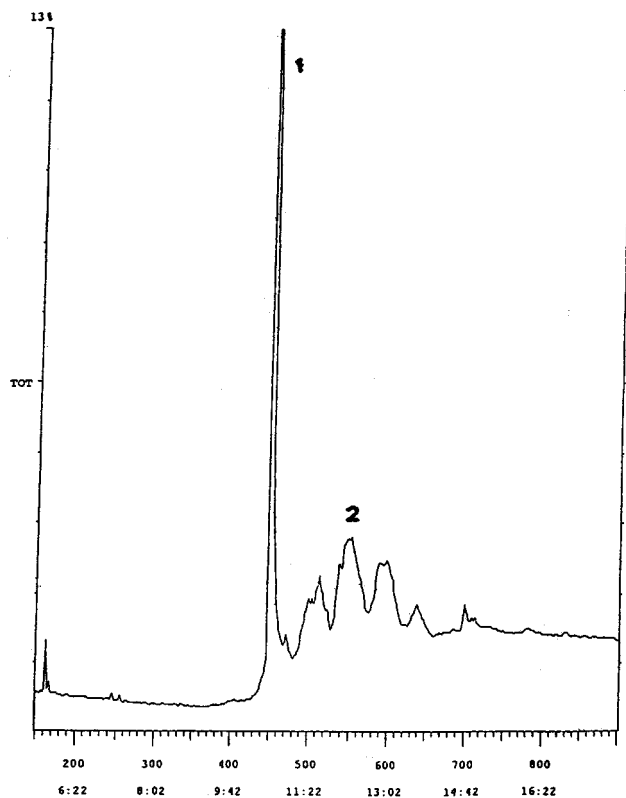


Figure 3. GC-MS chromatogram of CH_2Cl_2 extract "B type 1 (new)": (1) diisobutyl phthalate; (2) chloroparaffins.

able in the extract from the corresponding used part; 3.2% in A Type 2 (new) and 105 ppm in the corresponding used part; 0.6% and 0.1% respectively in new and used B Type 2 extracts; 0.8% in Decanter Type 3 (new); 0.5% in Extractor (new) and undetectable in the corresponding used part; and 0.3% in Pump Gasket (used).

The fact that far larger quantities of plasticizers were extracted by dichloromethane from new parts compared with used ones suggests that these contaminants are extracted from the plastic components by the essential oils as the oil/water emulsions pass through the various phases of the production process. The mean levels (\pm SD) of contaminants (calculated from 10 independent analyses) extracted from the plastic material samples by the essential oils are reported in Table 2. The plasticizer residues found in these extracts frequently reached levels higher than 100 ppm. Indeed, in many cases the concentrations were so high that dilution of the extracts was necessary before the analyses could be made.

CONCLUSIONS

The qualitative and quantitative differences in plasticizer residues found in the essential oils analyzed in our earlier studies can probably be attributed to the different types of plastic components used in the industrial extraction of citrus essential oils. As can be seen from Table 1, some plastic components contain only bis(2-ethylhexyl) phthalate, whereas others contain chloroparaffins, diisobutyl phthalate, and bis(2-ethylhexyl) phthalate, and still others contain triaryl phosphates and phthalate esters. Some essential oil samples previously analyzed contained no plasticizer residues of any kind, but high levels of these contaminants were detected in other samples. It would seem that high levels of contamination occur in the early stages of use

of new plastic components and that the "washing" and diluting effects of large-scale production steadily minimize the degree of contamination of the oils.

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