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Simple and Sensitive Determination of *o*-Phenylphenol in Citrus Fruits Using Gas Chromatography with Atomic Emission or Mass Spectrometric Detection

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In this work, a simple and sensitive method for the analysis of the pesticide *o*-phenylphenol (OPP) on citrus fruits was developed. OPP is extracted with dichloromethane by ultrasonication and derivatized with ferrocenecarboxylic acid chloride. Using ferrocene as a label, residues of OPP are determined by gas chromatography with atomic emission detection in the iron selective mode or with mass spectrometric detection. Sample cleanup is simple and rapid and merely involves a removal of excess reagent on an alumina minicolumn. The method detection limit is 2 ng of OPP/g of fruit, and recoveries from lemon samples fortified at levels of 35 and 140 ng/g are 101 and 106%, respectively. The citrus fruits analyzed (oranges, grapefruits, lemons) contained between 60 ng/g and 0.37 μg/g OPP (RSD = 8−13%), and the results were in good agreement with results obtained when OPP was analyzed using an established HPLC-FLD method. Several alcohols could also be identified in the fruit peel.

KEYWORDS: ***o*-Phenylphenol; citrus fruit; GC-AED; GC-MS; ferrocene carboxylic acid esters**

INTRODUCTION

o-Phenylphenol (OPP) is a widely used fungicide, especially for the postharvest treatment of citrus fruits to protect them from decay during transport and storage. However, OPP is suspected to be potentially carcinogenic, and induced disturbance of growth, a decrease in fertility, and kidney damage have been shown to occur in animal experiments (*1*). In Germany, the tolerance level for residues on citrus fruit is 12 mg/kg of whole fruit (*2*), in agreement with the European Union levels, but the treatment has to be indicated and the treated peels are declared unfit for consumption.

Residue analysis should provide low detection limits as well as good precision and accuracy. At the same time a simple and rapid method is required to prevent the distribution of harmful products. Several methods have been published to determine OPP residues on citrus fruits. Such methods include liquid chromatography (LC) with fluorescence (FLD) (*3*−*6*), electrochemical (*7*), or mass selective detection (MSD) (*8*) and gas chromatography (GC) (sometimes after derivatization) with flame ionization (*9*) or MSD (*10*−*12*). However, most of the published methods require a long and laborious sample preparation as well as large sample amounts due to their low sensitivity and selectivity. For example, naturally occurring fluorescence from citrus fruit components often interferes with the detection of fungicides in LC-FLD. Only LC-MSD provides low detection limits and little sample cleanup but, on the other hand, requires fairly expensive instrumentation. Another disadvantage of LC methods for OPP is that they usually require time-consuming external calibration runs. In GC, underivatized phenols tend to show peak tailing, and interference from matrix compounds is also common. Time-consuming steps such as steam distillation, liquid−liquid extraction, or column chromatography are often required for a sufficient sample cleanup.

Rolfes and Andersson (*13*) have developed a very sensitive and selective method to analyze phenols as ferrocenecarboxylic acid esters (FE) based on GC with atomic emission detection (AED) in the iron selective mode. Iron has excellent detection characteristics in AED: it can be detected down to 50 fg/s and has a selectivity versus carbon of 4.6×10^6 (*14*). Because volatile iron-containing compounds are not naturally present, underivatized matrix compounds do not interfere. The derivatization reaction is fast at room temperature, and sample cleanup involves no more than a filtration over aluminum oxide. We have now applied this derivatization procedure to the analysis of trace residues of OPP on citrus fruits. Instead of GC-AED, GC-MS can also be used to analyze the derivatized sample in cases when maximum sensitivity is not needed. This detection technique has the advantage that alcohol and phenol FEs can be distinguished easily due to their characteristic fragmentation patterns so that the two detection modes are complementary. Here we show how OPP can be rapidly and sensitively analyzed by GC-AED or GC-MS and how naturally occurring alcohols in the citrus peels can be analyzed qualitatively in the same run as the phenols by GC-MS.

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MATERIALS AND METHODS

Reagents and Chemicals. Dichloromethane for residue analysis (Acros, Geel, Belgium) was purified by percolation through activated aluminum oxide before use. The cyclohexane (Acros) used is of residue analysis grade. For HPLC, methanol pro analysi (Acros), purified water prepared with a Milli-Q water purification system (Millipore, Bedford, MA), and a 20 mL Chem Elut cartridge (Varian, Darmstadt, Germany) for cleanup were used. *o*-Phenylphenol (>99%, Merck, Darmstadt, Germany) and *o*-benzylphenol (99%, Aldrich, Taufkirchen, Germany) were employed as standards. Further chemicals used were anhydrous sodium sulfate (>99%, Fluka, St. Gallen, Switzerland), 4-(dimethylamino)pyridine (99%, Acros), and ferrocenecarboxylic acid chloride (synthesized following the procedure described in ref *15*); may be stored at −18 °C under argon for 1 year). Aluminum oxide (Fluka) was activated at 450 °C, deactivated with water, and stored at 160 °C for at least 24 h for a water content of 1.2% water.

Apparatus. The Agilent GC-AED system consists of a 6890N GC and a G2350A AED, equipped with a 30 m × 0.25 mm i.d. × 0.25 μm DB5-ms column (J&W Scientific, Folsom, CA), a Gerstel MPS2 autosampler, and a Gerstel CIS-Injector (Gerstel, Mülheim, Germany). The oven temperature was programmed as follows: 60 °C starting temperature, kept for 0.5 min, temperature ramp at 45 °C/min to 295 °C, then at 2 °C/min to 300 °C, kept for 3 min. Other GC-AED conditions were as follows: injector initial temperature, 60 °C, heated at 12 °C/s to 300 °C; helium carrier gas with 40 cm/s constant velocity; transfer line and cavity temperatures, 300 °C. Helium makeup flow for the AED is 240 mL/min; hydrogen and oxygen plasma gas pressures are 15 and 20 psi, respectively.

The ion trap GC-MS consists of a Finnigan MAT ion trap GCQ, fitted with a 30 m × 0.25 mm i.d. × 0.25 μm DB17-ms column (J&W Scientific), operated with EI ionization at 70 eV in full scan mode from 100 to 500 amu. The oven temperature was programmed as above, but with a 40 °C/min first temperature ramp, followed by 6 min at 300 °C. Other conditions were as follows: split/splitless injector used in the splitless mode at 250 °C (1 min); helium carrier gas at 40 cm/s constant velocity; transfer line temperature, 275 °C; ion source temperature, 200 °C; filament offset, 5 min. The tandem-quadrupole GC-MS consists of an Agilent 6890 GC with a 30 m × 0.32 mm × 0.25 μm HP5 column (Agilent) and a Waters Micromass (Manchester, U.K.) Quattro Micro mass spectrometer. It is operated in SIR mode on *m*/*z* 213 with EI ionization (70 eV). The temperature program was modified to a 30 °C/min ramp, followed by 4 min at 300 °C. Other conditions were the same as above.

For HPLC-FLD, a Hewlett-Packard 1100 HPLC system with a diode array and FLD detector is used, equipped with a C_{18} column (LiChrospher 60 RP-select B from Merck, 125 × 4 mm, 5 μm particle size) at 25 °C. Mobile phases A and B were phosphate buffer, pH 7.0 (352 mg of KH_2PO_4 + 726 mg of $Na_2HPO_4 \cdot 2\ H_2O$ in 1 L of twice distilled water), and methanol, respectively, using a gradient from 45% B at 0 min to 73% B at 20 min, and then a second gradient to 85% B at 24 min, which was kept isocratic for 10 min, followed by a gradient back to the initial 45% B at 40 min with a flow rate of 1.1 mL/min. The injection volume was 10 μL. Fluorescence detection was carried out with $\lambda_{ex} = 275$ nm and $\lambda_{em} = 330$ nm. External calibration was done with six standard solutions, ranging in concentration from 0.05 to 1.0 mg/L OPP in methanol.

Sample Preparation. A scheme of the procedure is presented in **Figure 1**. The sample fruits were purchased in supermarkets in Münster, Germany. The fruits were weighed and then peeled manually using gloves to avoid contamination. For the depth profile, an orange containing 1.5 μg of OPP/g peel was peeled manually in three layers (0.5−1.5 mm thick), and each of the layers was analyzed separately. The peel was crushed and homogenized with a household hand-held blender and then stored at −18 °C if not used immediately.

Approximately 3 g of peel is spiked with 10 nmol of *o*-benzylphenol (OBP) (100 μL of a 100 μM solution in toluene) as internal standard, and after 10 min has been allowed for evaporation of the solvent, the sample is extracted twice with dichloromethane (DCM) using ultrasonication (the first time with 20 mL of DCM, and the second time with 15 mL; each time, 15 min of ultrasonication). The suspension is decanted over glass wool into a 50 mL volumetric flask, and the residue is washed with DCM to yield 50 mL of extract, before anhydrous sodium sulfate is added to the combined extracts to remove residues of water. About 5 mL of the sample is then derivatized by adding 11 mg of ferrocenecarboxylic acid chloride (FCC) and 15 mg of 4-(dimethylamino)pyridine (DMAP) as catalyst. After a reaction time of 10 min at room temperature, the excess reagents are removed on an aluminum oxide minicolumn (1.7 g of aluminum oxide in a 3 mL SPE glass cartridge, packed under DCM). FEs are eluted with 3 mL of DCM. One and a half milliliters of the derivatized sample is transferred to a vial and concentrated almost to dryness using a gentle flow of nitrogen at 40 °C and finally dissolved in cyclohexane (1 mL for GC-AED or 50 μL for GC-MSD). The derivatives are stable for several months at 5 °C.

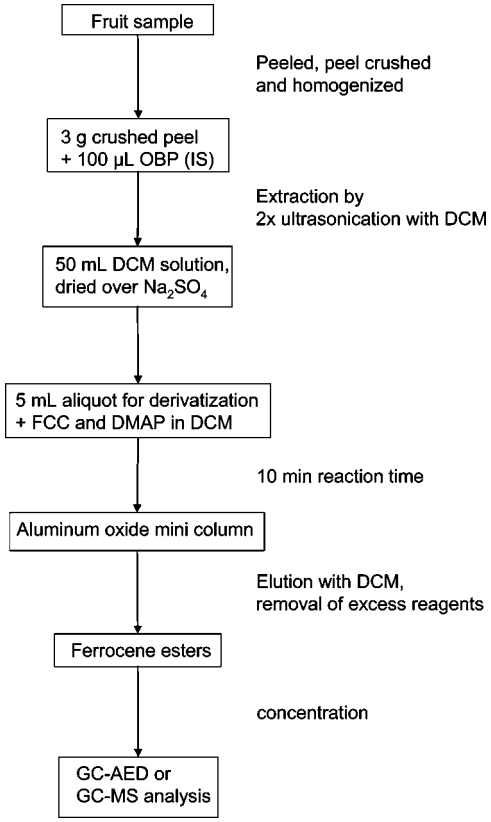

Figure 1. Analysis scheme.

Samples for recovery experiments were prepared by fortifying 3 g of crushed peel with 50 μL of a 50 μM or 100 μL of a 100 μM OPP standard solution in toluene (resulting in 35 or 140 ng of OPP/g of fruit, respectively). The sample was kept at room temperature for 10 min to let the solvent evaporate and was then extracted with DCM as described above. Two and a half nanomoles of 2-fluorophenol ferrocenecarboxylic acid ester (2FPE) in toluene (25 μL of a 100 μM solution) was added as a second internal standard after the alumina column separation to quantify losses during sample preparation. The limit of detection was determined by spiking the peel of an untreated lemon with decreasing amounts of a 1 μM OPP solution.

Sample Preparation for HPLC-FLD (*16*). Ten grams of homogenized peel is ultrasonicated with 100 mL of cyclohexane/ethyl acetate (1:1 v/v) for 5 min and then centrifuged for 5 min at 3000 rpm. The organic layer is decanted, and then the extraction is repeated with 50 mL of the same solvent mixture. The combined organic phase is concentrated using the rotary evaporator and adjusted to 20 mL. A 15 mL portion of the extract is cleaned up on a 20 mL Chem Elut cartridge, using 75 mL of cyclohexane/ethyl acetate to elute the analytes. After the addition of 1 mL of 5% ammonia, the sample is concentrated almost to dryness using a rotary evaporator and diluted with methanol to 10 mL. The extract is filtered through a 45 μm membrane filter before injection onto the column.

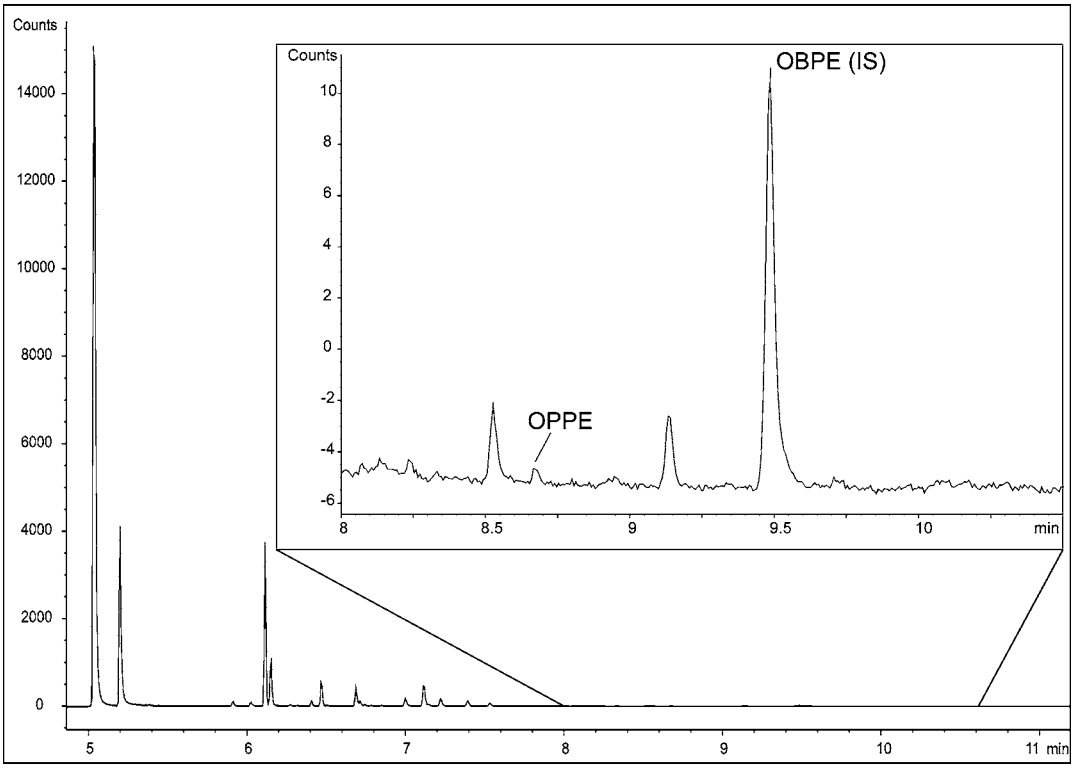

Figure 2. GC-AED chromatogram of the extract of a lemon spiked with 2 ng/g of fruit of OPP, which is the limit of detection.

RESULTS AND DISCUSSION

Method Development. Initially, 2FPE and 4-fluoro-2-methylphenol ferrocenecarboxylic acid ester (4F2MPE) were used as internal standards. Fluorinated compounds are very well suited as internal standards for different kinds of analytes, for example, polycyclic aromatic compounds (*17*), and we have found the fluorophenols to be highly useful for the analysis of alkylphenols in petroleum samples. However, 4F2MPE was found to partly coelute with 1-octanol-FE, which is an alcohol abundantly present in citrus peels, so that another internal standard had to be found. 2FPE has a much shorter retention time and consequently a higher volatility than OPPE, and in addition it shows a somewhat different polarity. Although very useful for the analysis of alkylphenols, it was therefore not a very good choice for the analysis of OPP. The commercially available OBP was instead chosen as the internal standard in this work. The retention time of the OBP ester (OBPE) is only 0.8 min longer than that of OPPE under the GC conditions used here, and no coelution was found with matrix components in any of the citrus samples analyzed. It is chemically very similar to OPP and is therefore expected to closely mirror the behavior of OPP, making it an ideal internal standard. Both phenols are derivatized with yields of >90% (determined after derivatization of the target analytes with 2FPE as internal standard). With OBP as the internal standard, the reproducibility of the procedure was increased significantly.

For the extraction of OPP from the peels, several techniques have been described. We investigated a combined steam distillation and liquid−liquid extraction with cyclohexane (using a modified Clevenger apparatus) as recommended in ref *9*. This Clevenger extraction is time-consuming and labor-intensive (2 h of reflux, manual liquid−liquid extraction), and in grapefruit extraction the results occasionally deviated from the results obtained with both HPLC-FLD and GC-AED following ultrasonication. The completeness of the ultrasonic extraction was checked by subjecting extracted grapefruit peels to a subsequent Clevenger extraction; only traces of additional OPPE were recovered. Ultrasonication with DCM was selected as the routine extraction method because the results were in agreement with the results obtained with the established HPLC method and because the recovery experiments showed recoveries close to 100%. Only for liquid samples such as pulp and juice was the Clevenger extraction applied because for these matrixes the organic layer of the DCM extract could not be separated sufficiently well from the aqueous phase.

The extraction of OPP from citrus peels with DCM and ultrasonication was investigated in detail. One 10 min ultrasonication proved not to be satisfactory because up to 20% of the original OPP content was found in a second extract gained in the same way. When the extraction time was increased to 2 × 15 min, only traces of OPP were left in the residue.

Finally, the GC temperature program was optimized for short analysis time and sharp OPPE and OBPE peaks. Best results were obtained with the steep temperature ramp described under Materials and Methods, which allows a complete GC run to be performed in just over 11 min while maintaining good resolution for the analytes and narrow peak widths.

Limit of Detection (LOD) and Linear Range. The LOD of the GC-AED of 3 fmol of iron (S/N = 3, measured with pure OPPE standards) would translate into a LOD of ≈1.4 ng of OPP/g of fruit (depending on the thickness of the peel and the exact sample size). The linear working range of the instrument from 6 to >12000 fmol ($R^2 = 0.9996$) would cover OPP contents in the range from 3 ng to >6 μg/g of fruit. For higher contents, 1 μL instead of 2 μL should be injected. However, the LOD determined by spiking an untreated fruit is 2 ng/g of fruit if a S/N of 2 is used (as suggested in ref *18*), as shown in **Figure 2**. With a definition of S/N = 3, the detection limit is 3 ng/g of fruit. The detection limit for samples is about

Table 1. Recovery of OPP from Lemons Measured with 2-Benzylphenol (2BP) as First Internal Standard (IS) (Added before Sample Preparation) and 2-Fluorophenol (2FPE) as Second Internal Standard (Added after Sample Preparation)

OPP spiked (ng/g)	recovery based on 2BP as IS (%)	RSD (%) ($n = 3$)	recovery based on 2FPE as IS (%)	RSD (%) ($n = 3$)
35	101	8	86	9
140	106	3	94	6

twice the detection limit of pure standards because of a somewhat noisier background caused by the fruit matrix.

The detection limit of the ion trap GC-MS instrument for OPP in spiked citrus fruits is 35 ng/g of fruit (S/N = 3). The response factor of OBPE with respect to OPPE for quantification was determined by injecting 20 pmol (10 μM solution in cyclohexane) of the standards. It was found to be 0.98 (RSD 5%, $n = 6$) when quantification is done using the base peak of *m*/*z* 213. The linear working range of the tandem-quadrupole instrument from 50 fmol to 90000 fmol ($R^2 = 0.998$) translates into OPP contents between 9 ng/g and 15 μg/g of fruit.

Recovery from Spiked Samples. The peel of one batch of untreated lemons was used for recovery experiments after the absence of OPP residues was confirmed by analysis. The reagent and solvent blank levels for OPP were below detection limit. Two fortification levels in the same range as found on treated citrus fruits were analyzed three times each (see **Table 1**).

Comparison of Results with GC-MS and HPLC. The peel of different fruits (grapefruits, oranges, and lemons) were extracted several times each and analyzed by GC-AED following the described procedure. In the case of the orange, three oranges from the same batch were analyzed twice each. The results are summarized in **Table 2**. OPP contents between 0.06 and 0.37 μg/g of whole fruit were found with a standard deviation of 7−13%. A major contributing factor to the standard deviation is probably an inhomogeneous distribution of OPP on the peel, which makes it necessary not to use a too small sample size. A chromatogram of a grapefruit extract is presented as an example in **Figure 3**. The derivatized extracts were also concentrated further and injected into both ion trap and tandem-quadrupole GC-MS, yielding similar results (**Table 2**).

For validation of the GC-AED and GC-MS methods, the same grapefruit and the two previously analyzed lemons were subjected to an HPLC-FLD analysis including a different extraction procedure (see Materials and Methods), based on a validated analytical procedure (*16*). The results were in good agreement with the results obtained by GC-AED and GC-MS, as shown in **Table 2**.

Depth Profile in an Orange Peel. This experiment was carried out to examine the penetration of OPP into the peel of a treated fruit. Results can be reported only semiquantitatively

Table 2. Comparison of OPP Contents in Several Fruits Obtained with the Different Methods

	GC-AED			GC-MS ion trap			GC-MS quadrupole			HPLC–FLD		
fruit	OPP (μg/g)	*n*	RSD (%)	OPP (μg/g)	*n*	RSD (%)	OPP (μg/g)	*n*	RSD (%)	OPP (μg/g)	*n*	RSD (%)
orange	0.37	6	8	0.32	5	10	0.34	2		nd		
grapefruit	0.23	5	7	0.24	1		0.26	1		0.23	2	
lemon 1	0.28	5	13	0.26	2		0.34	1		0.35	1	
lemon 2	0.06	2		<LOQ	1		nd			0.06	1	

[a] Amounts calculated per gram of whole fruit. nd, not determined.

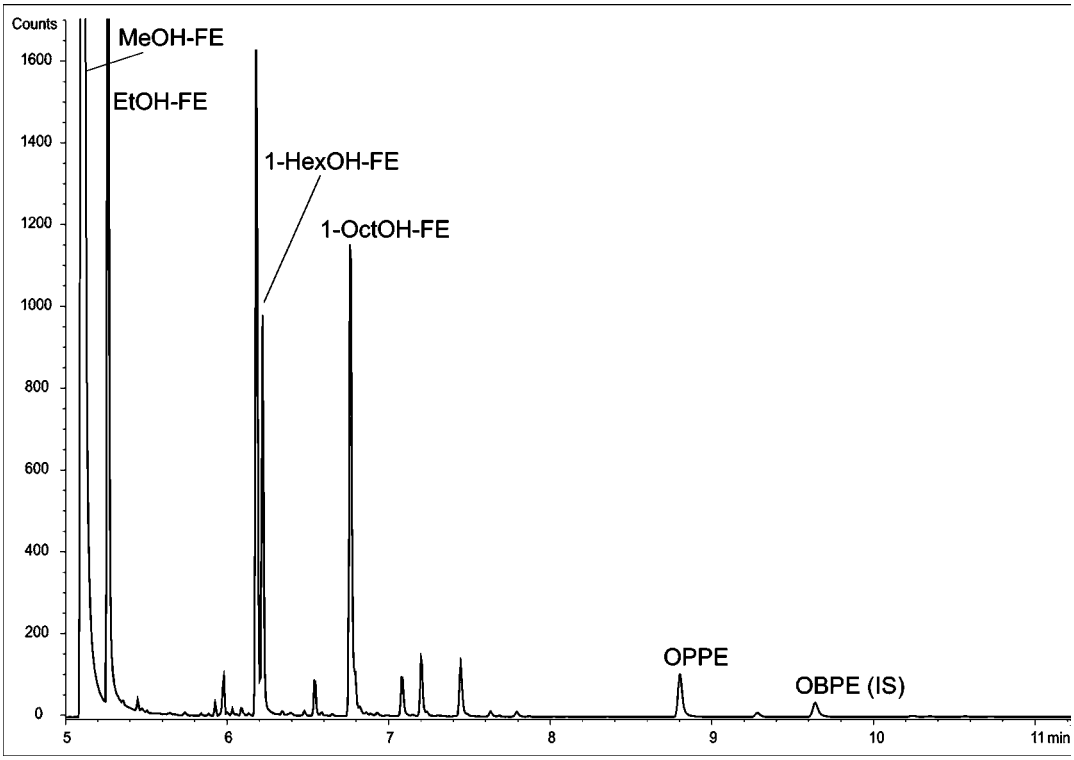

Figure 3. GC-AED chromatogram of a grapefruit extract with a determined OPP content of 236 ng/g of fruit.

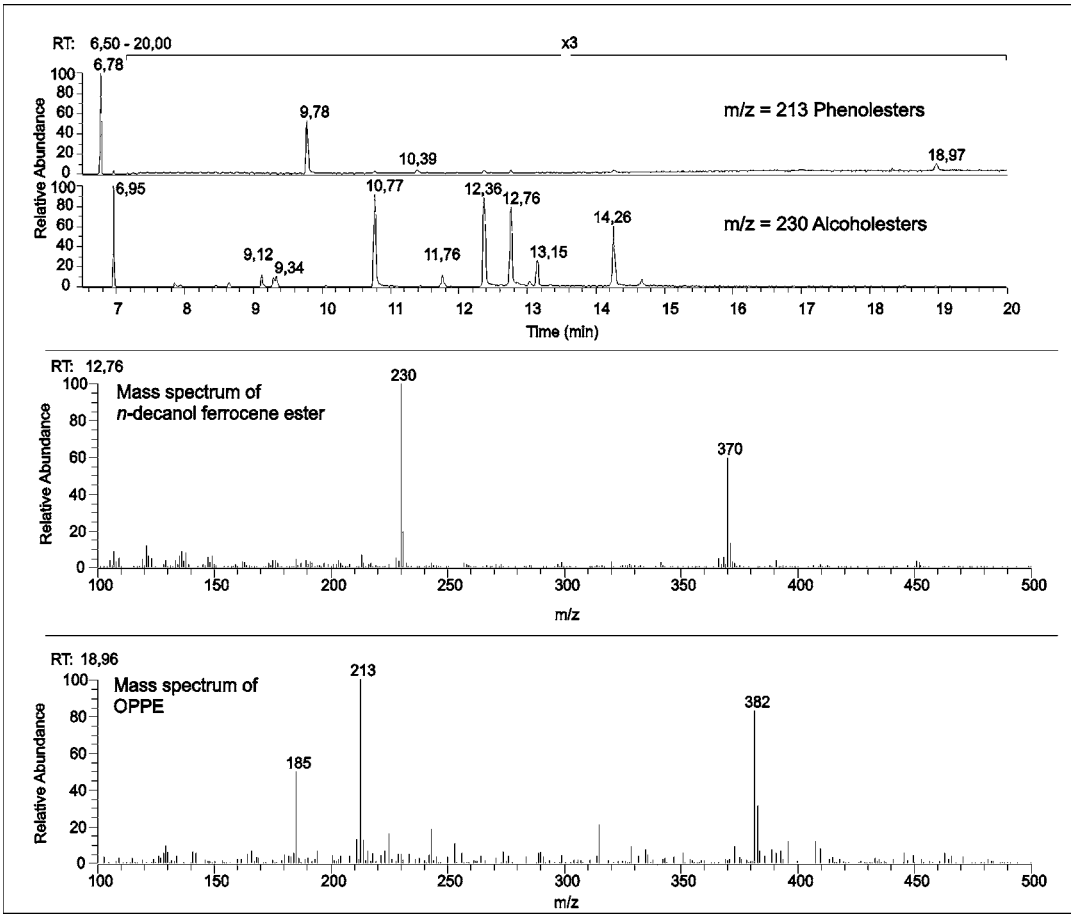

Figure 4. GC-MS chromatogram (extracted ion chromatogram) of an orange extract, including mass spectra of *n*-decanol-FE (retention time = 12.76 min) and OPPE (retention time = 18.97 min).

due to the uncertainty of the manual peeling process. However, the concentration of OPP was found to decrease rapidly from the outer peel to the pulp, yielding about 4.4 μg/g in the outer layer (exocarp), 1.8 μg/g in the middle layer (inner exocarp), and 0.3 μg/g in the inner layer (mesocarp) of the analyzed orange peel (see **Figure 4**). The pulp was also analyzed and found to contain OPP at the detection limit of 2 ng/g. It can be concluded that the consumption of peeled fruits that have been treated with OPP does not lead to a significant intake of the pesticide.

Identification of Alcohols in Citrus Peels. Apart from the M^+ ion, the mass spectra of alcohol ferrocenecarboxylic acid esters show a fragment of *m*/*z* 230 corresponding to the ferrocenecarboxylic acid cation as the base peak. In contrast to that, phenol esters show (besides M^+) a base peak of *m*/*z* 213 corresponding to the ferrocenecarbonyl cation, and *m*/*z* 230 is absent (*19*). In all cases M^+ is prominent (but never the base ion) so that it can be used for aiding in the identification of the compound. Therefore, the two single ions 213 and 230 in a GC-MS run can be used to construct alcohol- and phenol-selective chromatograms, respectively. A range of *n*-alcohols up to undecanol could be identified in all analyzed citrus fruits by comparison of retention times with those of standards and by their mass spectral data as illustrated in **Figure 4**. Methanol is usually the most abundant alcohol (see **Figure 3**, at levels in the low micrograms per gram range, which is >100 times the methanol blank level), especially in grapefruit peels. Methanol has not been reported in citrus fruit peels in the literature so far, probably due to its high volatility when measured without derivatization. Also, ethanol, *n*-hexanol, and *n*-octanol are common. In lemons and oranges, citronellol (3,7-dimethyloct-6-en-1-ol) can be found in large quantities. Unsaturated or alicyclic C_6- and C_{10}-alcohols were also found, one of them possibly being nerol or geraniol. All of these alcohols are reported previously in the literature as constituents of citrus peels, for example, in ref *20*. A list of the alcohols identified in an orange peel is included in **Table 3**. The derivatization yield has not been checked for alcohols but varies more than that among the phenols. Secondary alcohols generally show a lower yield of ester than primary alcohols so that at the moment the alcohols can be analyzed in only a qualitative sense.

Table 3. Identification of Alcohols and Phenols in an Orange Peel by GC-MS (See **Figure 5**)

retention time (min)	M^+	major fragments	substance	identification by standards
6.78	244		methanol-FE	yes
6.95	258	230	ethanol-FE	yes
9.12	314	230	*n*-hexanol-FE	yes
9.34	312	230	C_6-alcohol-FE[a]	
9.78	294	213, 185	?	
10.77	342	230	*n*-octanol-FE	yes
11.39	324	213, 185	2FPE (IS)	
11.76	356	230	nonanol-FE	
12.36	368	230, 320	citronellol-FE + ?	yes
12.76	370	230	*n*-decanol-FE	yes
13.15	366	230	C_{10}-alcohol-FE[a]	
14.26	364	230	C_{10}-alcohol-FE[a]	
18.97	382	213, 185	OPPE	yes

[a] Alicyclic or unsaturated.

Conclusions. A fast and sensitive GC method for the determination of OPP on citrus fruit peels was developed and tested for different fruit samples. The derivatization with ferrocenecarboxylic acid has the advantage that the analysis can be performed either with atomic emission or mass selective detection. GC-AED is the more sensitive technique with a detection limit of 2 ng/g OPP and is therefore used for low concentrations. GC-MS is excellent for distinguishing between alcohols and phenols, and because it gives the molecular mass of each ester, it can be used in the identification of unknown components as well as to indicate possible coelution. Small sample sizes down to a few milligrams of peel (depending on the amount of OPP) may be analyzed, although a standard sample size of 3 g is recommended for a better homogeneity and representativeness. The sample preparation utilizing ultrasonic extraction and derivatization takes ≈2.5 h. The GC run takes only 11 min, and no calibration runs are needed as quantification is done with an internal standard.

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