$CHCl_3$ was also confirmed in one soft drink subsample. Good agreement was obtained between full-scan electron impact mass spectra for analytes and standards. Because concentrations of approximately 50 ng/g were necessary for GC–MS confirmation, other residues found in the subsamples or composites could not be confirmed.

CONCLUSIONS

The compositing technique studied allows screening (quick semiquantitative analysis) for VHCs in a wide variety of foods. For composites I and X, the compositing technique provides quantitative information. However, the losses of analytes during preparation or compositing of foods for composites II and XII permit only qualitative information to be obtained; individual foods must be analyzed if quantitative data are desired. Careful attention to sample preparation is necessary to ensure similar partitioning characteristics for VHC determination in the heterogeneous food composites.

VHCs were detected at ppb levels in a variety of the foods collected; the compounds found, as well as their levels, differed from sample to sample. Because of the limited sampling, no conclusions regarding the general magnitude of VHC residues in foods should be drawn.

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Determination of Volatile Aldehydes in Meat as 2,4-Dinitrophenylhydrazones Using Reversed-Phase High-Performance Liquid Chromatography

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Volatile aldehydes formed by oxidative degradation of unsaturated fatty acids were isolated from meat and determined as 2,4-dinitrophenylhydrazones (DNPHs). Meat samples were homogenized in ethanol and the volatile aldehydes distilled under vacuum into a trap filled with 2,4-dinitrophenylhydrazine. The derivatization took place in a two-phase reaction with acidic ethanol solution and hexane. The recovery of aldehydes with more than five carbon atoms is better than 80% at trace concentrations (micrograms per gram). Determination is carried out by reversed-phase HPLC on C_{18}-RP columns with the eluent acetonitrile–water–tetrahydrofuran (75:24:1) at 50 °C using photometric detection at 360 nm. The HPLC method was optimized for the determination of volatile aldehydes formed during oxidative degradation of the unsaturated fatty acids occurring in food. The detection limit at 360 nm was found to be 5 pmol. The utility of the method for the detection of beginning oxidative rancidity was demonstrated with a storage experiment of frozen pork liver.

Low concentrations of aldehydes are found in most foods. Aldehydes are characterized by very low olfactory threshold concentrations and for this reason constitute important components of the natural flavor of a food. In fat-containing foods, these components of the flavor are formed during maturation by enzymatic and nonenzymatic reactions, preferentially by oxidation of unsaturated fatty acids (Ohloff, 1973; Tressl et al., 1975). In the course of storage, these reactions may result in a elevated formation of aldehydes, which then would represent typical components of the off-flavor. A particularly well-known off-flavor is rancidity, which is mainly due to the formation of carbonyl compounds as a consequence of the autoxidation of fatty acids (Grosch, 1975).

Two different methods are employed in the analytical detection of aldehydes in low, however, relevant concentrations in foods. In the first one, the carbonyl compounds are concentrated together with all volatile ingredients of the food sample with subsequent gas chromatographic separation and determination. The other method consists in a reaction with 2,4-dinitrophenylhydrazine (2,4-DNP) and chromatographic determination of the hydrazones. Owing to the high extinction coefficient of the 2,4-dinitrophenylhydrazones (2,4-DNPHs), photometric detection permits an identification of aldehydes in the nanogram range. Additionally, 2,4-DNPHs are well accessible to methods of separation by thin-layer and liquid chromatography.

Direct derivative formation in an acid aqueous solution has been used first for preparative reactions with oxo compounds. At the low concentrations as common in the analytical field, however, a yield of the corresponding 2,4-DNPHs of only 70% was found (Selim, 1977). Fur-

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thermore, under such conditions, hydroperoxides will be decomposed into carbonyl compounds (Horikx, 1964). For the purpose of forming derivatives of carbonyl compounds at trace concentrations in fat-containing foods, a direct method developed by Schwartz et al. (1963) using reagent-coated Celite has been used by numerous authors (Moerck and Ball, 1979; Caporaso and Sink, 1978; Sink and Smith, 1972; Wang and Odell, 1972; Dwivedi and Kinsella, 1974; Brown et al., 1973). Recently, Pradel and Adda (1980) have pointed out that application of this method may result in an elevated aldehyde content as a consequence of peroxide breakdown. Selim (1977) succeeded in obtaining a quantitative derivative formation from low aldehyde concentrations by using a two-phase mixture. This principle was selected and optimized for the purpose of our study. To avoid a direct contact of the acid reactant solution with hydroperoxides, we separated the aldehydes from the meat matrix by means of vacuum distillation.

The separation of the hydrazones of saturated, monounsaturated and diunsaturated aldehydes was performed by reversed-phase high-performance liquid chromatography (Reindl and Stan, 1982). The method described here was developed in particular for a quantitative determination of all aldehydes in the relevant trace range that are characteristic for the off-flavor formation in foods.

EXPERIMENTAL SECTION

Chemicals. Ethanol, *n*-hexane, acetonitrile, tetrahydrofurane, methanol, sodium borohydride, and 2,4-dinitrophenylhydrazine were z. A. quality for Merck, Darmstadt, West Germany. Fatty acid methyl esters were of highest purity availlable; oleic acid methyl ester (GC reference substance from Merck); linoleic acid methyl ester and linoleic acid methyl ester (Fluka, Buchs, Switzerland, puriss.); arachidonic acid methyl ester (Fluka purum). All aldehydes were purchased from Atlanta, Heidelberg, West Germany: pentanal; hexanal; *trans*-2-hexenal; *trans*,-*trans*-2,4-heptadienal; *trans*-2-heptenal; heptanal; *trans*-2-octenal; octanal; *trans*,*trans*-2,4-nonadienal; *trans*-2-nonenal; nonanal; decanal; *trans*,*trans*-2,4-decadienal; *trans*-2-decenal.

Water was highly purified by the equipment of Millipore Corp., Bedford, MA. Ethanol was purified by adding 1 g of sodium borohydride to 1 L and distilling after 2 h. Hexane was purified in the same way by the addition of 1 g of sodium borohydride in 50 mL of ethanol to 1 L of *n*-hexane and fractional distillation. All solvents used for HPLC were filtered through fiber glass filters, 0.7 μm; water was Chrom AR quality form Promochem, Wesel, West Germany.

Standards. The 2,4-DNPHs were prepared as reference compounds by reacting about 0.5 g of the aldehyde with a solution of 2 g of 2,4-DNP in 30% sulfuric acid.

Analytical Procedure. A sample of 5–10 g of meat was homogenized with 50 mL of cold ethanol in a mixer with glass mount. The homogenate was transferred into centrifuge tubes by rinsing the mixing vessel with 10 mL of ethanol. The homogenate was centrifuged immediately in a refrigerated centrifuge (0 °C) at 900*g* for 10 min. The supernatant was distilled under vacuum (20–30 torr) in a rotary evaporator at a water bath temperature of 50 °C. The condenser was cooled to 0 °C. After the first distillation was finished, 50 mL of water was added and a second distillation performed with an elevated water bath temperature of 65 °C. The distillate receiver was filled with 45 mL of 2,4-DNP solution [1 g of 2,4-DNP in a 1-L $HCl–H_3PO_4$ mixture (1:1) diluted to pH 1]. The rotary evaporator was connected by means of a short vacuum hose to a wash bottle also containing 45 mL of 2,4-DNP solution. Upon termination of the distillation the 2,4-DNP solutions were united in a 250-mL Erlenmeyer flask and kept for 1 h at room temperature in the dark (aluminum foil). To this solution 50 mL of *n*-hexane was added and the mixture was stirred for 2 h by using a magnetic stirrer. Care must be taken to ensure a vigorous mixing of both phases. Then the hexane phase was separated in a separatory funnel and washed twice with 10 mL of water to remove the acid. After this the solvent was removed at 30 °C by using water jet vacuum. The dry residue was dissolved in 2 mL of methanol for HPLC analysis. The purity of the reagents was checked by a blank value.

Scheme I

LIVER
↓ homogenization
↓ extraction with purified ethanol
HOMOGENATE
↓ cooling
↓ centrifugation (900 G)
SUPERNATANT
↓ vacuumdistillation
↓ derivate formation
2,4-DNP AND 2,4-DNPHs
↓ extraction with n-hexane
2,4-DNPHs
↓ HPLC seperation
↓ on C_{18}- reversed phase
2,4-DNPH

High-Performance Liquid Chromatography (HPLC). HPLC equipment consisted of a Spectra-Physics 8700 HPLC pump with helium eluent degassing (Spectra-Physics, Santa Clara, CA), an automatic sample applicator, Kipp Model 9209 (Kipp-Analytica, Emmen, Netherlands), with Rheodyne sample valve, No. 70–10 (Rheodyne, Cotati, CA), a column oven, Knauer type 89.00 (Knauer, Berlin, West Germany), and a variable-wavelength detector, Perkin-Elmer LC 55 (Perkin-Elmer, Überlingen, West Germany). An integrator HP 3390 A (Hewlett-Packard, Avondale, PA) was used for the calculation of peak areas. The 2,4-DNPHs were separated in a 4.6 mm × 250 mm Supelcosil LC 18 column, 5 μm (Supelco Inc., Belefonte, PA), with isocratic elution of 1.0 mL/min. Injector and main column were interconnected by means of a 30-mm protective column with LiChrosorb RP 8, 5 μm (Merck). The eluent consisted of acetonitrile–water–tetrahydrofuran at a ratio of 75:24:1 (v/v/v). The eluent was heated up in a preceding 100-mm column with LiChroprep RP 18 (Merck) installed between the pump and injector. The temperature of all columns was 50 °C. The injected volume was 20 μL and detection took place at 360 nm.

RESULTS AND DISCUSSION

The samples were prepared in such a way as to ensure a separation of the complete aldehyde fraction from the complex matrix under mild conditions (see Scheme I). Particularly, the formation of artifacts from hydroperoxides of the fatty acids had to be avoided. The best method to achieve this was a combination of solvent extraction (ethanol) and vacuum steam distillation. The use of ethanol resulted in an inactivation of all enzymes in the food samples, a denaturation of proteins, and a complete extraction of aldehydes. The aldehydes were separated from the ethanol extract by means of vacuum steam distillation at temperatures not exceeding 22–25 °C. Distillation as described took approximately 25 min. In accordance with the results of Grosch (1968) the formation of carbonyls from hydroperoxides could be minimized.

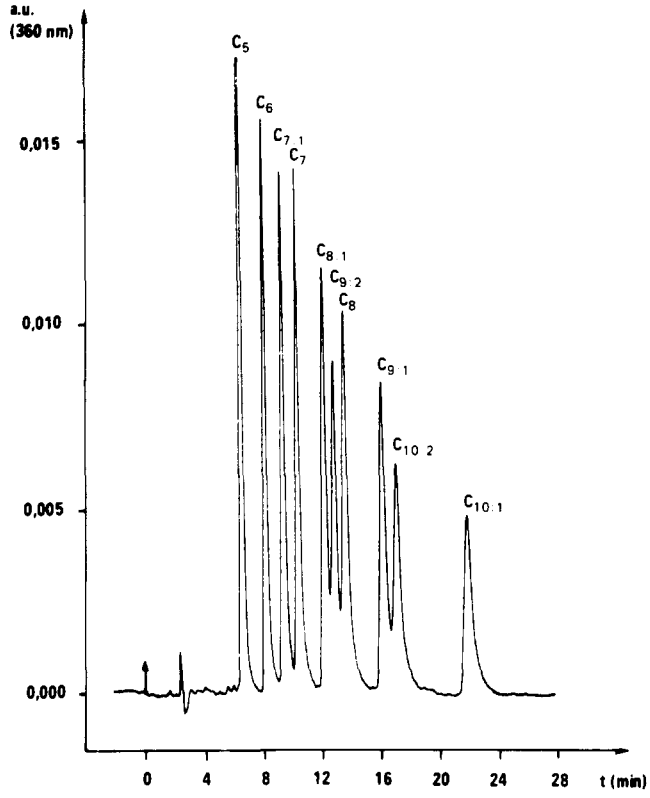

Figure 1. RP-HPLC of 2,4-DNPHs from straight-chain aliphatic aldehydes. The test mixture contains 80 ng of each aldehyde; only pentanal was 100 ng.

Distillation took place in a two-step procedure. First, ethanol was removed by distillation and then water was added. Only in this way could foaming within the distillation flask be avoided. Using defoaming agents Jeon et al. (1976) observed an occurrence of a variety of substances (e.g., silicones) that certainly would interfere with our extraction procedure and HPLC determination. The use of the purified solvents, ethanol and water, minimized the risk of contamination of the samples.

By use of the two-phase system as described, a derivative formation of approximately 100% could be achieved for aldehydes with more than five C atoms after a 3-h reaction period. This may be explained by the distribution coefficient that assigns the preferential dissolution of the 2,4-DNPHs in the nonpolar phase. The derivatization reaction is taking place in the aqueous phase through proton catalysis. Continued extraction of the hydrazones formed from the aqueous phase will result in a complete derivative formation. An experimental series using hexanal as the model substance served to optimize the conditions for reaction (leaving for 1 h and stirring for 2 h). Following separation of the two phases, the hexane phase was washed with water to remove acid and 2,4-DNP residues. At this step, there will also be a partial loss of lower carbonyl hydrazones (C_1–C_4), which, however, is unimportant for the purposes of this study. These carbonyls are not indicative for lipid oxidation, because they are formed also from other precursors such as amino acids and carbohydrates. The washing procedure enhances the stability of the formed hydrazones during storage until chromatographic analysis, because it removes remaining acid from the organic phase. Traces of acid may catalyze the decomposition of 2,4-DNPHs. Samples may be stored in the refrigerator for several weeks.

The chromatographic system of separation was designed to enable the detection of the aldehydes which theoretically were expected to form as a consequence of lipid oxidation

Table I. Analytical Recoveries for Three Selected Aldehydes

aldehyde	recovery, %[a]
hexanal	85
2-octenal	81
2,4-decadienal	85

[a] Tested with 5 μg of aldehyde each in fresh liver following the procedure described under Experimental Section.

Table II. Reproducibility for Three Selected Aldehydes from Eight Determinations

aldehyde	added μg	$\bar{x}$ found, μg	SD, μg	RSD, %
hexanal	8.4	7.1	0.13	1.8
2-octenal	7.3	5.9	0.10	1.7
2,4-decadienal	9.0	7.7	0.27	3.5

(Badings, 1970; Hoffmann and Meijboom, 1968; Meijboom and Jongenotter, 1971). A description and discussion of the chromatographic method are published elsewhere (Reindl and Stan, 1982). Figure 1 provides a chromatogram of the reference aldehydes of interest, demonstrating their separation as 2,4-DNPHs in the order of their elution: pentanal, C_5; hexanal, C_6; 2-heptenal, $C_{7:1}$; heptanal, C_7; 2-octenal, $C_{8:1}$; 2,4-nonadienal, $C_{9:2}$; octanal, C_8; 2-nonenal, $C_{9:1}$; 2,4-decadienal, $C_{10:2}$; 2-decenal, $C_{10:1}$. Quantitative analysis of the 2,4-DNPHs consists in a measurement of absorption at 360 nm. A linear calibration curve was found for quantities between 5 pmol and 3 nmol corresponding to 2 ng and 1 μg of hydrazones.

Reproducibility of the method is indicated in Table I. For these experiments hexanal served as the representative alkanal, 2-octenal as alkenal, and 2,4-decadienal as alkadienal. By this mixture the most important distillation range of the aldehydes searched for was covered. Recovery rates were established by adding the three above-mentioned aldehydes to liver homogenate (Table II). For calibration external standards of varying concentrations were used. A suitable aldehyde as an internal standard would be difficult to find and may cause problems of stability against oxidation at the low concentration which is necessary for this purpose.

The recovery experiments shown in Table II demonstrate the utility of the method for the determination of the stage of autoxidation in progress. By use of the method and equipment as described, the detection limit was found to be about 5 pmol of 2,4-DNPH for all aldehydes studied. This corresponds, e.g., for hexanal to 2 ng of 2,4-DNPH and 0.5 ng of aldehyde, respectively. On the condition of a corresponding optimization and detection of only one or two aldehydes, the detection limit e.g., for hexanal and heptanal may be brought down to 0.1 ng of aldehyde.

In a model experiment, aldehydes from the autoxidation of individual fatty acids were determined. The experiment involved the methyl esters of oleic, linoleic, linolenic, and arachidonic acid. The experiment was based on an initial amount of 0.5 g of each fatty acid methyl ester that had been stored in sealed ground-neck round-bottom flasks at room temperature and exposed to light for 1 week. According to Badings (1970), varying and in part characteristic patterns would have to be expected for the carbonyls formed. Figure 2 illustrates the carbonyl products of the autoxidation of the fatty acid methyl esters. The most abundant aldehydes have been marked accordingly to the model of the reference aldehydes. All aldehydes were confirmed by mass spectrometry as their DNPH. Only two peaks were not yet identified. The qualitative

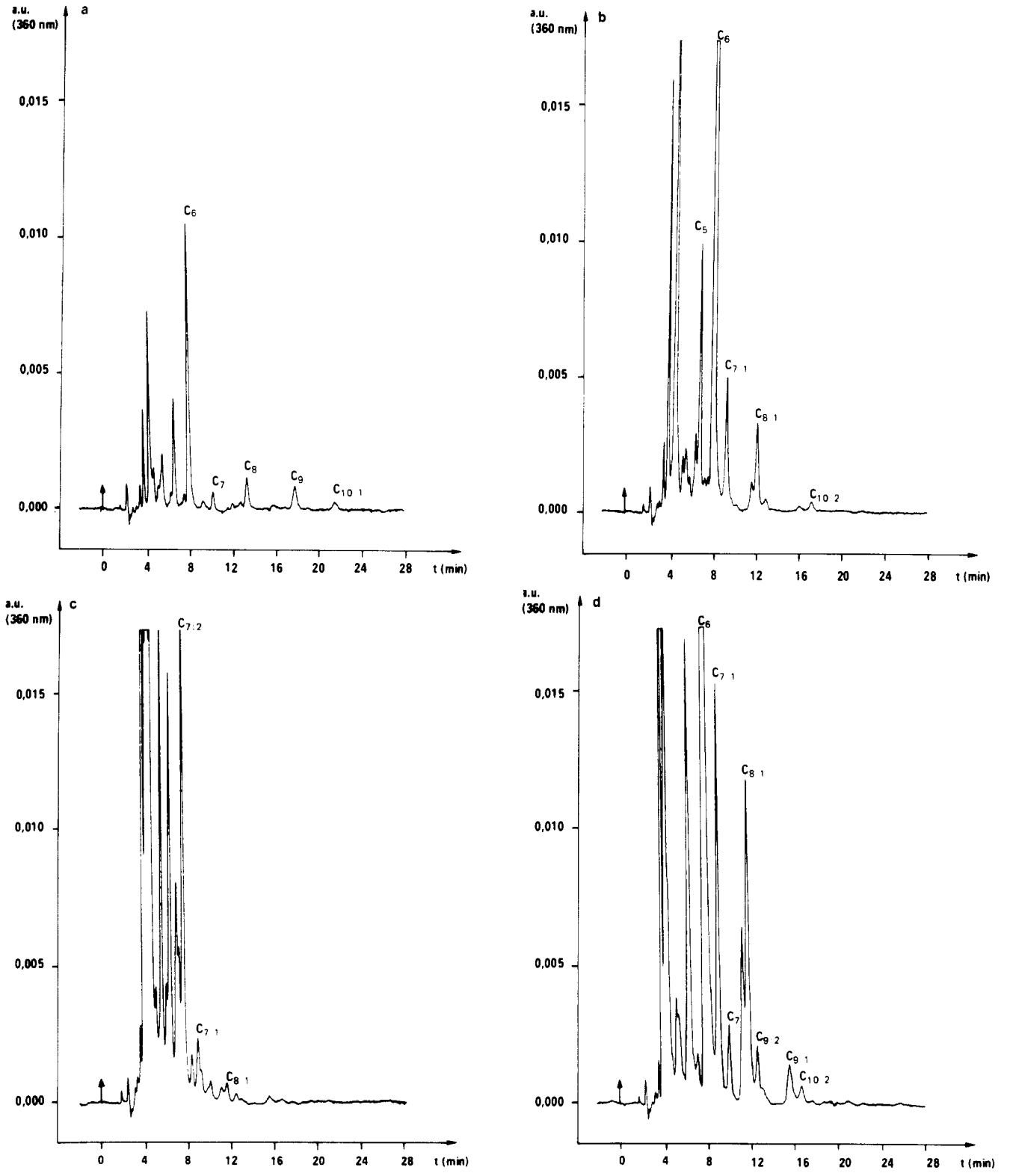

Figure 2. HPLC of volatile carbonyls from autoxidized fatty acids: (a) methyl oleate; (b) methyl linoleate; (c) methyl linolenate; (d) methyl arachidonate.

aldehyde compositions for the individual fatty acid methyl esters were coincident with literature data (Parsons, 1974). However, quantitative determination and comparison with the corresponding literature data (Parsons, 1974; Henderson et al., 1980) revealed differences that may be explained by the different conditions of oxidation. On the other hand, Schieberle and Grosch (1981) have shown unsaturated aldehydes, in particular 2-octenal and 2,4-decadienal, to continue with decomposition, resulting in hexanal as the major end product. Owing to the conditions of oxidation, higher aldehydes (C_8 and above) will not occur in such amounts as in the event of the frequently described primary breakdown of hydroperoxides (Parsons, 1974).

In addition to hexanal being the main product from oleic, linoleic, and arachidonic acid, the high heptadienal content resulting from the oxidation of linoleinic acid is a striking feature. Other characteristics are a considerable formation of octanal and nonanal from oleic acid, the absences of heptanal in the case of linoleic acid and that of 2-nonenal and 2,4-decadienal from oleic acid as well as an obvious production of 2,4-nonadienal from arachidonic acid. In this way the chromatographic data also permit

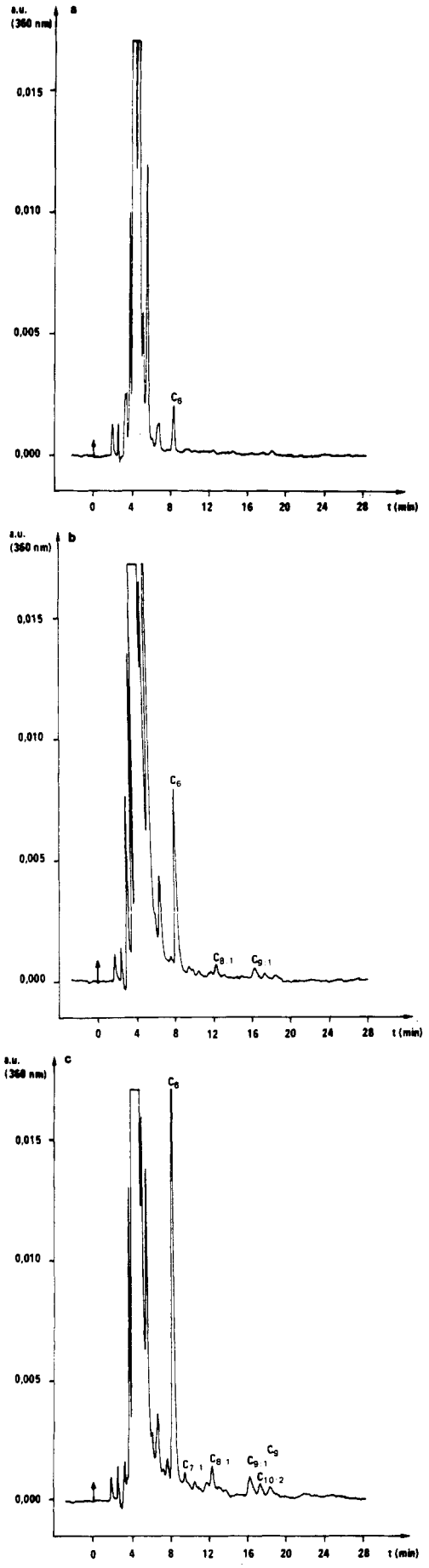

Figure 3. HPLC of volatile carbonyls from frozen pork liver in a storage experiment: (a) 1 week at −18 °C; (b) 4 months at −18 °C; (c) 4 months at −8 °C.

inferences as to the involvement of individual fatty acids in the lipid oxidation within complex matrices.

The described method was applied within a study of the temperature dependency of the storability of pork liver. Some examples from this work were selected to demonstrate the application of the analytical procedure in food samples. The detailed results of the study will be published elsewhere. In Figure 3 the aldehyde content of stored liver samples is given as 2,4-DNPHs. The pork livers were cut into equal pieces of about 8 g fresh weight, put into commonly used polyethylene bags (50-μm foil thickness) of appropriate size, and heat sealed. These samples were frozen under controlled conditions and stored at −8 and −18 °C (±0.7 °C), respectively. It becomes evident from the chromatograms that hexanal formation was the most important parameter. After 1 week of storage at −28 °C, a hexanal content of 0.04 mg/kg (0.14 μmol/kg) was measured. After 4 months at −18 °C, the respective figures were 0.18 mg/kg (0.64 μmol/kg) and after 4 months at −8 °C 0.65 mg/kg (2.3 μmol/kg). Additionally, the quantities of other carbonylic oxidation products have to be evaluated. The involvement of the individual fatty acids in lipid oxidation can be recognized if the composition of fatty acids is known. In the case of liver, oleic, linoleic, and arachidonic acids are the most abundant unsaturated fatty acids as was found by gas chromatographic lipid analysis (our results, unpublished). It is seen from Figure 3 that at the beginning of the storage experiment practically no lipid oxidation could be observed. After 4 months of storage, however, the detected aldehyde spectra make the conclusion plausible that all three unsaturated fatty acids occurring in pork liver participate in the autoxidation reactions.

At the higher storage temperature of −8 °C several aldehydes characteristic for oxidative rancidity clearly exceed the analytical detection limit. The occurrence of these other rancidity aldehydes supports the conclusion drawn from the increasing hexanal content. They are therefore of considerable importance for the early chemical detection of rancidity. The analytical procedure described was designed to detect low-degree oxidative fat deterioration in frozen meat. We hope that we were able to demonstrate with the examples shown in Figure 3 the utility of our method for this purpose and more generally for the detection of autoxidation of unsaturated fatty acids in biological and food matrices of various origin.

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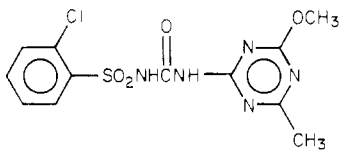
Analysis of the Herbicide Chlorsulfuron in Soil by Liquid Chromatography

Edward W. Zahnow

An analytical method based on the use of a liquid chromatograph and a photoconductivity detector is described for chlorsulfuron, 2-chloro-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzenesulfonamide, previously known as DPX-W4189, which is the active ingredient in Du Pont Glean Weed Killer. As little as 100 pg can be detected and measured after passage through the chromatographic column. Coupled with extraction, cleanup, and isolation procedures, the method provides a means of determining chlorsulfuron in soil at levels as low as 200 pg/g (0.2 ppb).

Du Pont Glean Weed Killer is effective in controlling a variety of weeds common to cereal grain fields without causing injury to the crop plants themselves. The active ingredient, chlorsulfuron, 2-chloro-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide, is a sulfonylurea of the structure



chlorsulfuron

The synthesis and toxicology of this compound have been described by Levitt et al. (1981), and these authors also include the results of both pre- and postemergence tests on a wide variety of weeds commonly associated with cereal crops.

Glean is usually applied at very low levels, with a range of 10–40 g/ha being fairly typical on fields of wheat, oats, and barley. Since the half-life in soil of the active ingredient, chlorsulfuron, is approximately 1 month during the growing season, it is apparent that the residues of chlorsulfuron in the soil will be extremely low.

Consequently, a method has been developed that can be used to measure chlorsulfuron in soil with a detection limit of 200 pg/g (0.2 ppb). Derivatization of chlorsulfuron is not required, and the operating conditions are sufficiently mild that decomposition is avoided.

A literature search revealed a number of methods that can be used for the analysis of sulfonylureas. If gas chromatography is to be used for the analysis, the sulfonylureas must be derivatized to more volatile and stable compounds by reacting the polar NH groups with dimethyl sulfate, methyl iodide, or diazomethane. Derivatization with diazomethane has been reported by Braselton et al. (1975, 1976, 1977), Midha et al. (1976), Taylor (1972), and Taylor et al. (1977). Maeda et al. (1981) have demonstrated that sulfonylureas can be determined by methylation with diazomethane followed by acylation with heptafluorobutyric anhydride. The use of dimethyl sulfate is described by Kleber et al. (1977), Prescott and Redman (1972), Sabih (1970), Sabih and Sabih (1976), and Simons et al. (1972). An extractive methylation involving methyl iodide in methylene chloride is given in the paper by Hartvig et al. (1980).

Methods for sulfonylureas based on liquid chromatography have been reported by Beyer (1972), Harzer (1980), Molins et al. (1975), Robertson et al. (1979), Sved et al. (1976), Uihlein and Sistovaris (1982), Waahlin-Boll and Melander (1979), and Weber (1976). Both normal and reverse-phase systems have been used, and it is not necessary to form derivatives since sulfonylureas generally give adequate response with ultraviolet absorbance detectors. Besenfelder (1981) has reported an improvement in sensitivity based on precolumn derivatization and fluorometric detection. However, the sensitivity requirements for chlorsulfuron in soil are much greater than normally encountered, and in addition, extraction procedures used for soil analysis liberate substantial quantities of UV-absorbing substances from soil that interfere with the chlorsulfuron determination.

To obtain adequate sensitivity and also eliminate undesirable responses from coextracted materials, use is made of the photoconductivity detector that is described in detail by Popovich et al. (1979). An application of this detector is discussed by McKinley (1981). The photoconductivity detector is selective for molecules containing sulfur, halogen, nitrogen, and phosphorus atoms. Its sensitivity for chlorsulfuron is 15 times greater than can be achieved with

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