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Volatile Halocarbons in Butter: Elevated Tetrachloroethylene Levels in Samples Obtained in Close Proximity to Dry-Cleaning Establishments

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In recent years there has been increasing public concern that the chemical products and by-products of our industrialized society may be contaminating both our environment and our food supply. Materials not directly associated with food production, such as polychlorinated and brominated biphenyls, have been found in foods. According to the criteria described by Jelinek (1981) to evaluate the likelihood for a chemical to contaminate food, which include production volume, toxicity, toxic by-products, solubility behavior, environmental stability, patterns of end use, and means of disposal, the volatile halocarbons (VHCs) were selected as target compounds in an examination for potential contaminants in selected foods. Chosen for this survey were chloroform, carbon tetrachloride, trichloroethylene, bromodichloromethane, methylchloroform, and tetrachloroethylene, frequently referred to as perchloroethylene (PCE).

Because of their volatility, VHCs are suitable for determination by headspace gas chromatography using an electron-capture detector (ECD). This technique for VHCs has used internal or external standards as well as the method of standard additions (Entz and Hollifield 1982). With the advent of automated headspace analyzers, such as the Perkin-Elmer HS-100 autosampler mated to a Sigma 2000 gas chromatograph, the technique of multiple headspace extraction (MHE) has been found advantageous (Kolb et al. 1984). MHE was used in this study to minimize sample handling, and thereby reduce the potential for laboratory contamination and maximize throughput.

Recently this laboratory reported findings of several VHCs in margarine, including PCE in four samples at levels above the usual background findings (Entz and Diachenko 1988). Those samples had been obtained from a food store located immediately next to a dry-cleaning establishment. Follow-up investigation was conducted to determine the frequency of occurrence and

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levels of PCE that may be present in fatty foods purchased from stores located both near and distant from dry cleaners. Butter was chosen as a model food because it is a highly uniform product of very high fat content, which would be expected to act as a good absorber of the lipophilic VHCs. Furthermore, butter is most frequently wrapped in waxed paper or foil-covered sticks which are not packaged in sealed cans or plastic wraps that exclude ambient air. Butters were purchased from food stores located next to dry cleaners, stores one or two doors removed from dry cleaners, and stores located where there were no dry cleaners in the vicinity. This paper presents results of these analyses and correlations between level of VHCs in butter and the proximity to dry cleaners of the food store where the butter was purchased.

MATERIALS AND METHODS

The MHE analyses were performed with a Perkin-Elmer HS-100 automated headspace analyzer coupled to a Perkin-Elmer Sigma 2000 gas chromatograph equipped with a ^{63}Ni ECD. The output signal from the gas chromatograph was fed directly to an IBM 9000 scientific computer where the chromatograms were acquired and integrated by using the IBM Chromatography Applications Program/Multichannel software (Release 1.3). Gas chromatography/mass spectrometry was performed on a Finnigan 4000 quadrupole mass spectrometer in the electron ionization mode. Glass screw-cap vials (0.5 dram) with PTFE-lined septa (Supelco, Inc., Bellefonte, PA) were used to store standards. Standard solutions were withdrawn through the septa of these vials by a microliter syringe. The test materials were sealed and equilibrated in 22-mL glass vials (Perkin-Elmer Corp., Norwalk, CT). Vials were sealed by using PTFE-lined septa with a crimp-top retainer. All reagents, glassware, and septa were examined by the procedure to ensure that none of the analytes were present in these components.

Standard solutions were prepared by weighing neat compounds (>95% purity) in a volumetric flask and diluting with high-purity grade methanol (Burdick & Jackson Laboratories Inc., Muskegon, MI) by the method of Entz and Hollifield (1982). These standards were pipetted from microliter syringes into volumetric flasks and further diluted with methanol to obtain the working standard solutions.

Butters were obtained from retail outlets, placed in polyethylene bags, and stored in a freezer. One 0.25-pound stick of butter from each retail package was placed in a beaker and softened to approximately room temperature (<30°C) on a hot plate at low heat only until the softened semisolid could be mixed thoroughly (Entz and Diachenko 1988; Uhler and Miller 1988). This procedure is identical to the validated margarine preparation procedure described by Entz and Diachenko (1988). The butters were then placed in 40-mL screw-cap vials with PTFE-lined caps and stored in a freezer. These storage vials were allowed to equilibrate to room temperature before a portion of butter was removed for analysis.

Butter portions of 100-200 mg were weighed into tared crimp-top vials to which was added 2 µL (ca. 40 ng) of tetrachlorotetrafluoropropane as an internal retention-time standard and to monitor for leaking vials. With each set of test vials, a vial containing 2 µL of the mixed standard and 2 µL of the internal standard was used to serve as the calibration standard for the MHE determination. The HS-100 automatic headspace analyzer was programmed to operate in the MHE mode with five extractions from each vial. The vials were thermostated at 60°C for 30 min before each injection.

The transfer line from the HS-100 headspace analyzer to the Sigma 2000 gas chromatograph was maintained at 90°C. The detector was a ^{63}Ni ECD maintained at 300°C with argon-methane (95:5) used as a makeup gas set at a flow of 28 mL/min. The column was a fused silica capillary column, 30 m x 0.32 mm i.d., coated with bonded DB-5 at a film thickness of 1.0 µm. Helium carrier gas, with a linear velocity of 32 cm/s, was also used to pressurize (0.5 min) the test vial and make an injection of ca. 150 µL (0.10-min injection time). The gas chromatograph was programmed to maintain column oven temperature of 40°C for 11 min followed by a temperature increase of 20.0°C/min to 120°C, which was maintained for 2.0 min. The total run time was 17 min.

Sealed 22-mL vials containing the butters were thermostated for 30 min at 60°C. Manual injections were made by withdrawing 2-mL aliquots from the sealed vials with a gas-tight syringe. The 0.125-in. diameter stainless-steel column consisted of two segments, a 10-ft section packed with 20% SP-2100 + 0.1% Carbowax coated on 80/100 mesh Chromosorb W(HP) followed by a 2-ft section packed with 6% SE-30 also on Chromosorb W(HP). The mass spectrometer was operated in the multiple ion detection mode; the major ions monitored were m/z 61, 63, 97, 99, 117, and 119 for methylchloroform and m/z 129, 131, 133, 164, 166, and 168 for PCE. Mass spectrometry data were obtained for the volatile compounds from several selected butters. Identities of methylchloroform and PCE were confirmed in these butters and in a blank butter fortified with 204 ppb of methylchloroform and PCE.

Briefly, the MHE method consists of sealing a weighed portion of the test material in a vial with a septum lid. The vial is then thermostated, and a portion of the headspace is injected onto the gas-chromatographic column. Injections from this vial are repeated five times so that a set of data is obtained that represents the exponential decrease in analyte concentration with each subsequent headspace extraction. If enough extractions are made, the geometric progression derived by summing the peak areas of each extraction can be solved to yield: $A_T = A_1/(1 - e^{-k})$ where A_T is the total peak area, A_1 is the peak area for the first extraction, and $-k$ is the slope obtained by plotting $(n - 1)$ vs $\ln A_n$ where A_n is the peak area of the nth extraction of the analyte. The total peak area ($\underline{A}_T$) can be related to the quantitative amount of analyte in the sample. A more complete discussion and validation of this technique for butter may be found in the article by Uhler and Miller (1988).

RESULTS AND DISCUSSION

Forty-six butters collected from 14 retail outlets in the Washington, DC, area were examined to determine incidence and levels of VHCs and to follow up on previous findings of elevated PCE in margarines from a store located next to a dry-cleaning establishment. Examination of the butters showed that carbon tetrachloride, trichloroethylene, and bromodichloromethane were not present above their quantitation limits of 5, 15, and 12 ppb, respectively. Chloroform was found in all 46 butters at an average of 92 ppb (range 30-255 ppb). There was no discernible correlation between the level of chloroform found and such factors as the manufacturer of the butter or the location of the retail outlet from which the butter was purchased. It can be postulated that, since water contact occurs during the manufacture of butter, these chloroform levels may reflect the partition of chloroform from the process water used by the manufacturer. No further attempt was made to characterize the source of the chloroform because of the low levels found.

Several butters contained relatively high methylchloroform levels (10 had levels higher than 100 ppb and one contained 7,500 ppb). Because methylchloroform is used as a solvent in packaging adhesives (Entz and Diachenko 1988), it is possible that the methylchloroform residues may have resulted from the sealing of the cases with such adhesives. Some butters with high methylchloroform levels were the same brand and had similar manufacturing codes; they were imprinted with different dates but had the same letter code following the date. Discussion with the manufacturer revealed that these butters were produced from the same manufacturing plant and that the manufacturer was using a methylchloroform-based packaging adhesive. The use was subsequently discontinued. Later collections of butters with the same code letter did not have elevated levels of methylchloroform.

As suspected from the previous work by Entz and Diachenko (1988), butters obtained from stores located near dry-cleaning establishments contained elevated levels of PCE. This is consistent with a major use of PCE as a dry-cleaning solvent. These initial findings prompted us to obtain additional butters intentionally collected from food stores located both nearby and far removed from dry-cleaning establishments. We then collected butters at stores adjacent to dry-cleaning establishments and stores close to, but not next to, dry-cleaning establishments. Frequently in small suburban shopping centers, a food store was located with one or two stores between it and a dry-cleaning establishment, although both were in the same overall structure. Butters from these stores were grouped together in the "near dry

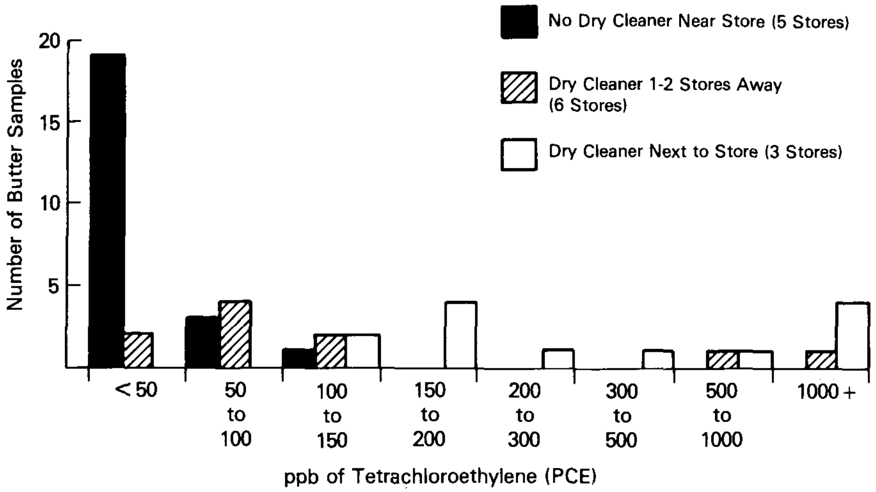

Figure 1. PCE concentration in butter purchased at different stores located at various distances from dry-cleaning establishments.

cleaners" category. These food stores included small convenience stores as well as large supermarkets.

Figure 1 shows the sampling site's proximity to a dry-cleaning establishment compared to the associated levels of PCE found in the butter. The level of PCE detected is graphically represented along the abscissa in arbitrary groupings of <50, 50 to 100, 100 to 150, 150 to 200, 200 to 300, 300 to 500, 500 to 1000, and >1000 ppb. The three bars in each grouping represent butters collected from stores with no dry-cleaning establishments in the vicinity, stores one to two stores removed from dry-cleaning establishments ("near dry cleaners"), and stores immediately adjoining dry-cleaning establishments. The number of butters in each grouping is represented along the ordinate.

The butters collected from stores with no dry-cleaning establishments nearby generally contained less than 50 ppb of PCE, although one contained 111 ppb. However, many of the butters from stores located near dry-cleaning establishments had elevated levels of PCE (100 to >1000 ppb). Generally butters from the stores located immediately next to dry-cleaning establishments had higher levels of PCE than those from stores which were one or two stores removed from dry-cleaning operations ("near dry cleaners"). These findings parallel a study conducted in the Netherlands in which the exhaled breath of people living in the same building above dry-cleaning establishments was shown to contain higher levels of PCE than the breath of people living next to dry-cleaning establishments. This study indicated that both groups of people were exposed to higher levels of PCE than are typically found in air samples when no dry-cleaning establishment is in the immediate area (World Health Organization 1984).

PCE has been found as a contaminant of butter, with elevated levels detected in samples obtained from retail outlets located next to or near dry cleaners. This association, combined with the widespread use of PCE as a dry-cleaning fluid that is usually discharged to the atmosphere, suggests that aerial transport of the vapors given off by the dry-cleaning process may be a potential source of PCE in butters collected from stores near dry-cleaning establishments.

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