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Investigation of Sulfur-Containing Components in Roasted Coffee

Roland Tressl* and Reinhard Silwar

By means of distillation–extraction, adsorption chromatography, and capillary gas chromatography–mass spectrometry, 23 sulfur components (mercaptans, sulfides, and di- and trisulfides) were characterized in roasted coffee. Fifteen components were identified for the first time and confirmed by synthesis (among them are sulfur-containing furans and two dithiolanes). The amounts of sulfur components were determined in roasted Arabica and Robusta coffees, as well as in instant coffee.

More than 100 sulfur-containing components (among them are mercaptans, sulfides, disulfides, thiophenes, and thiazoles) were identified in roasted coffee. Reichstein and Staudinger (1926) characterized furfurylmercaptan (2-furylmethanethiol) as an important aroma constituent of roasted coffee which is considered to be a character impact component (Ohloff and Flament, 1978). Kahweofuran (2-methyl-3-oxa-8-thiabicyclo[3.3.0]-1,4-octadiene) was isolated from coffee by Stoll et al. (1967) and its structure confirmed by synthesis (Büchi et al., 1971). According to Ohloff and Flament (1978), kahweofuran possesses a violent sulfury odor in the pure state and develops a pleasant roasted and smoky note in high dilution. Dimethyl sulfide, methyl ethyl sulfide, furfuryl methyl sulfide, 5-methylfurfuryl methyl sulfide, difurfuryl sulfide, and 15 thiophenes were characterized by Stoll et al. (1967). Vitzthum and Werkhoff (1974) detected 25 thiazoles in aroma concentrates from roasted coffee. In the present work, we report the identification and (semi)quantification of 23 mercaptans, sulfides, and di- and trisulfides in roasted Arabica and Robusta coffee. Fifteen components were characterized for the first time and their structures confirmed by synthesis.

Forschungsinstitut für Chemisch-technische Analyse, Technische Universität Berlin, D-1000 Berlin 65, West Germany.

EXPERIMENTAL SECTION

Materials. High-grown Arabica coffee of Columbian origin and Robusta coffees were roasted to a medium roast and stored in packages with an excess of air at 4 or 25 °C.

Isolation of Sulfur Components. One hundred grams of roasted coffee was ground and placed in a 2-L round-bottom flask containing 1 L of distilled water. The pH was 4.7–5.0. The volatiles were isolated by distillation–extraction (Schultz et al., 1977) with 100 mL of freshly distilled ether–pentane (1:1) for 2 h. The extract was dried over anhydrous Na_2SO_4, concentrated to a volume of 0.1 mL by using a special holdup Vigreux column, stored under nitrogen at −10 °C, and further separated by ad-

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Table I. Sulfur Components Characterized in Roasted Coffee

component	I_K	LSC	M+	m/e	first report in roasted coffee
1, dimethyl disulfide	1063	I	94	94, 79, 45, 46, 47, 61	*a, h*
2, dimethyl trisulfide	1361	I	126	45, 79, 47, 126, 46, 64, 61, 111	*h, j*
3, methyl ethyl trisulfide	1638	I	140	61, 45, 46, 47, 140, 79, 93, 64	*g, j*
4, 5-methyl-2-(methylthio)furan	1366	II	128	128, 85, 113, 45, 43, 69, 53, 51	*b, g*
5, 2-methyl-3-(methylthio)furan	1383	II	128	128, 113, 43, 99, 85, 51, 53, 69, 81	*g, j*
6, 2-methyl-3-(methyldithio)furan	1651	II	160	160, 113, 112, 43, 39, 85, 51, 69	*g, j*
7, 2,5-dimethyl-3-(methylthio)furan	1440	II	142	142, 127, 43, 99, 128, 85, 95, 53	*g, j*
8, 2,5-dimethyl-3-(methyldithio)furan	1762	II	174	43, 174, 127, 126, 128, 159, 95	*g, j*
9, 3,3′-dimethyl-1,2-dithiolane	1462	II	134	69, 41, 134, 59, 55, 64, 106, 78	*g, j*
10, 3,3′-dimethyl-4-oxo-1,2-dithiolane	1850	III	148	106, 78, 148, 41, 42, 60, 64	*g, j*
11, kahweofuran (2-methyl-3-oxa-8-thiabicyclo[3.3.0]-1,4-octadiene)	1753	II	140	140, 111, 97, 139, 43, 59, 77	*c*
12, homokahweofuran (2,4-dimethyl-3-oxa-8-thiabicyclo[3.3.0]-1,4-octadiene)	1779	II	154	139, 154, 77, 45, 53, 69, 97, 111	*i, j*
13, furfurylmercaptan	1431	II	114	81, 53, 114	*d, h*
14, furfuryl methyl sulfide	1465	II	128	81, 53, 128, 45, 113	*e, h*
15, furfuryl methyl disulfide	1770	II	160	81, 53, 160, 45, 64, 113	*f, h*
16, furfuryl methyl trisulfide		II	192	81, 45, 53, 192, 64, 113, 127, 160	*i, j*
17, furfuryl ethyl sulfide	1526	II	142	81, 53, 45, 142	*g, j*
18, difurfuryl sulfide	2178	II	194	81, 53, 45, 194, 113, 82	*f, g*
19, difurfuryl disulfide		II	226	81, 53, 45, 226	*g, j*
20, (5-methylfurfuryl)mercaptan	1473	II	128	95, 43, 51, 128, 51, 67, 81, 65	*g, j*
21, 5-methylfurfuryl methyl sulfide	1531	II	142	95, 43, 142, 51, 67, 81, 127	*f, g*
22, 5-methylfurfuryl methyl disulfide	1827	II	174	95, 43, 174, 51, 67, 81, 127, 113	*g, j*
23, 5-methylfurfuryl disulfide		II	254	95, 43, 127, 254, 128	*g, j*

[a] Stoffelsma et al. (1968). [b] Gautschi et al. (1967). [c] Büchi et al. (1971). [d] Reichstein and Staudinger (1926). [e] Gianturco et al. (1964). [f] Stoll et al. (1967). [g] Synthesized. [h] Commercially available. [i] Tentatively identified. [j] First reported in this work.

sorption chromatography. This sample preparation was repeated 10–20 times.

Adsorption Chromatography. A separation according to the polarity of components was carried out by liquid–solid chromatography. A 0.1-mL extract was separated on 3 g of silica gel 60 (activity II–III; Merck 7734; column 200 × 0.9 mm i.d.), and six fractions (40 mL each) with solvents of increasing polarity were eluated with (I) pentane, (II) pentane (P)–methylene chloride (MC) (4:1), (III) P–MC (1:1), (IV) P–MC (1:2), (V) P–ether, and (VI) ether. Fractions were concentrated to 0.1 mL and then analyzed by gas chromatography.

Preparative Gas Chromatography. Preparative investigations were performed with a Varian Aerograph 2740-1, equipped with an FID and an effluent splitter (10:1). Conditions were as follows: temperature program 60–230 °C, 4 °C/min; 3-m glass column (4-mm i.d.); 15% CW 20M on Chromosorb WAW/DMCS, 60–80 mesh; 60 mL of N_2/min (column A).

Capillary Gas Chromatography. *Column B.* For capillary GLC a 50-m (0.25-mm i.d.) glass capillary coated with CW 20M in a Carlo Erba Fractovap 2101 AC with an FID was used. Conditions were as follows: temperature program 70–180 °C, 2 °C/min; 3 mL of He/min.

Column C. A 25-m (0.30-mm i.d.) glass capillary coated with UCON HB 5100 in the same gas chromatograph, but equipped with an FPD for sulfur-selective analysis, was used. The gas chromatographic conditions were as described above.

Capillary Gas Chromatography–Mass Spectrometry. Capillary gas chromatographic–mass spectrometric conditions were as described by Tressl et al. (1978).

Synthesis of Reference Components. Some authentic samples of organic compounds were obtained from reliable commercial sources. The others were synthesized by well-established procedures. 2,5-Dimethyl-3-(methylthio)furan, 2-methyl-3-(methylthio)furan, and 5-methylfurfuryl methyl disulfide were synthesized by methylation of the mercaptans with diazomethane. 2,5-Dimethyl-3-(methyldithio)furan, 2-methyl-3-(methyldithio)furan, and 5-methylfurfuryl methyl disulfide were prepared by reacting the mercaptans with CH_3SCl (Brintzinger and Ellwanger, 1954). (5-Methylfurfuryl)mercaptan was synthesized according to the procedure of Kofod (1955) by reaction of 5-methylfurfuryl alcohol with thiourea. Difurfuryl disulfide and bis(5-methylfurfuryl) disulfide were formed by oxidation of the mercaptans with iodine as reported by McAllan et al. (1951). Difurfuryl sulfide was obtained by reaction of furfural with cysteine under roasting conditions. 3,3-Dimethyl-1,2-dithiolane was synthesized by cyclization of 1,3-dimercapto-3-methylbutane as described by Schöberl and Gräfje (1958). 3,3′-Dimethyl-1,2-dithiolan-4-one was prepared by reaction of 1,3-dibromo-3-methyl-2-butanone with Na_2S according to the method of Luhmann et al. (1977). Furfuryl ethyl sulfide was obtained by the reaction of ethyl iodide with an aqueous alkaline solution of furfurylmercaptan (McAllan et al., 1951).

RESULTS AND DISCUSSION

High-grown green Arabica coffees and Robusta coffees were roasted to a medium roast, ground, and packed with low air content. The volatiles were isolated by distillation–extraction (with pentane–ether during 2 h) and separated by means of adsorption chromatography according to the polarity of components. LSC fraction II possessed an intensive pleasant aroma of roasted coffee. By means of capillary gas chromatography–mass spectrometry, we characterized furan derivatives (among them are 2,2′-difurylmethane, 5-methyl-2-furfurylfuran, and 2,2′-difuryl- and 3-phenylfuran), more than 20 *N*-alkylpyrroles, 15 *N*-furfurylpyrroles (Tressl et al., 1981), and many sulfur-containing components. Figure 1 shows a capillary gas chromatogram of LSC fraction II with the major sulfur constituents. Individual components were isolated by preparative gas chromatography and characterized by mass

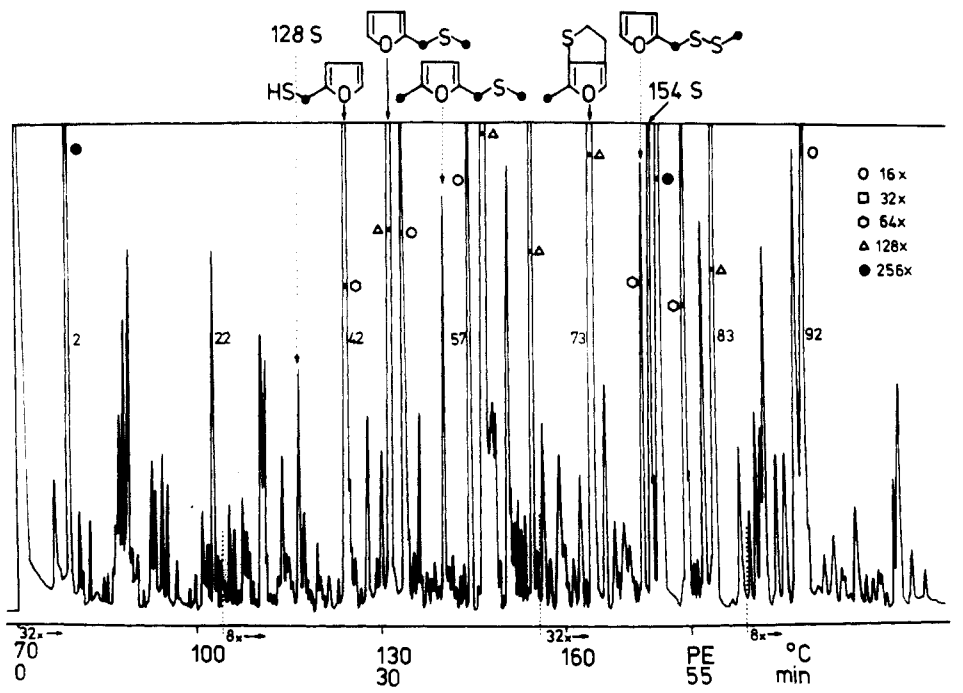

Figure 1. Capillary gas chromatogram of an Arabica coffee aroma extract (LSC fraction II).

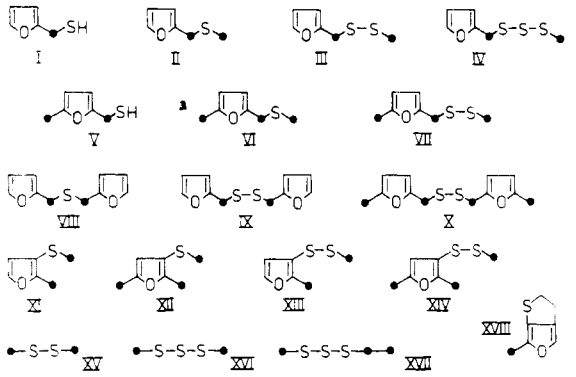

Figure 2. Sulfur components characterized in roasted coffee.

spectrometry. The identification was carried out by comparison of retentions and mass spectral data with synthesized reference samples. Table I presents Kovats' GLC indexes and mass spectra of 23 mercaptans, sulfides, and di- and trisulfides which were detected in roasted coffee. Fifteen components were characterized for the first time. Some of the components shown in Figure 2 indicate a possible formation from furfuraldehyde, cysteine, and methionine (components I–IV, VII, and VIII) and from 5-methylfurfuraldehyde, cysteine, and methionine (components V–VII and X), respectively. This has been proven in model reactions (Tressl et al., 1980). The disulfides and trisulfides were detected as trace components in fresh roasted coffee, and they increase in processed or stale coffee. Dimethyl disulfide and dimethyl trisulfide are known as the most important components in cooked cabbage and possess threshold values in water at 10 and 0.01 ppb. Both constituents increase in instant coffees. 2-Methyl-3-(methyldithio)furan and 2,5-dimethyl-3-(methyldithio)furan possess typical meaty/thiamine-like notes. 2-Methyl-3-thiofuran, 2,5-dimethyl-3-thiofuran, and additional derivates are known as synthetic meat flavor components (Evers, 1971; van den Ouweland and Peer, 1979).

3,3′-Dimethyl-1,2-dithiolane was synthesized from 3-methyl-2-buten-1-ol via 3-methyl-1,3-dithiol and purified by preparative gas chromatography. The mass spectrum

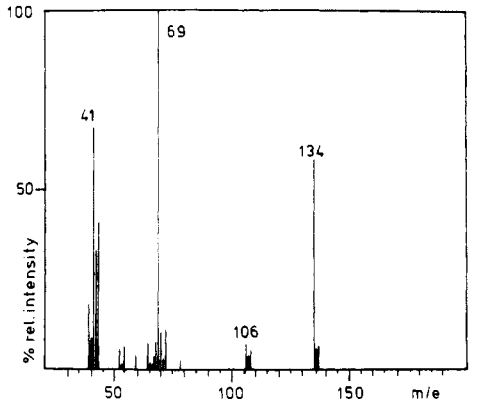

Figure 3. Mass spectrum of 3,3′-dimethyl-1,2-dithiolane.

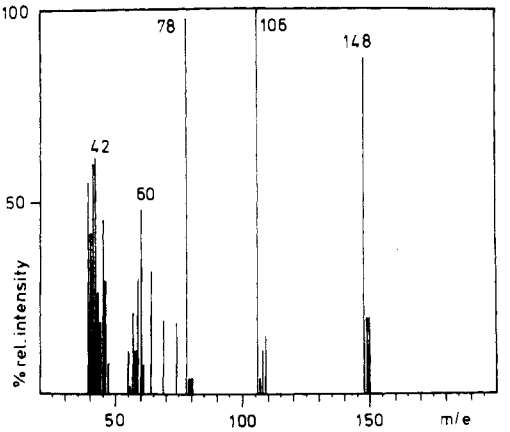

Figure 4. Mass spectrum of 3,3′-dimethyl-4-oxo-1,2-dithiolane.

is shown in Figure 3. The corresponding 4-oxo derivative was characterized as a major sulfur component in roasted coffee. The structure of component 10 was confirmed by synthesis. The mass spectrum of 3,3′-dimethyl-4-oxo-1,2-dithiolane is shown in Figure 4.

Figure 5 presents the amounts of sulfur-containing furans in medium-roasted Arabica and Robusta coffees. The investigation was carried out 10 days after roasting. Robusta coffees contain higher amounts of furfurylmercaptan,

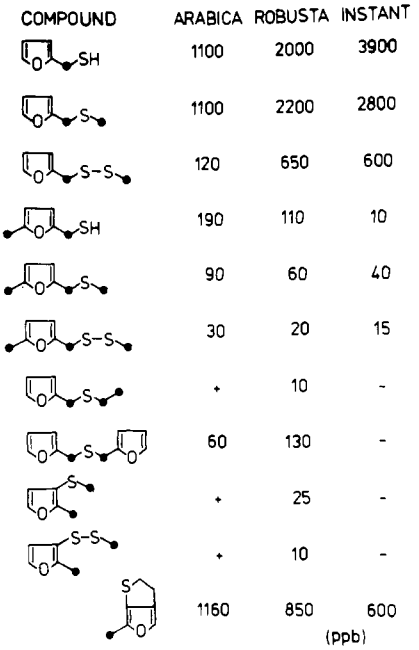

Figure 5. Sulfur-containing furans in Arabica and Robusta coffees.

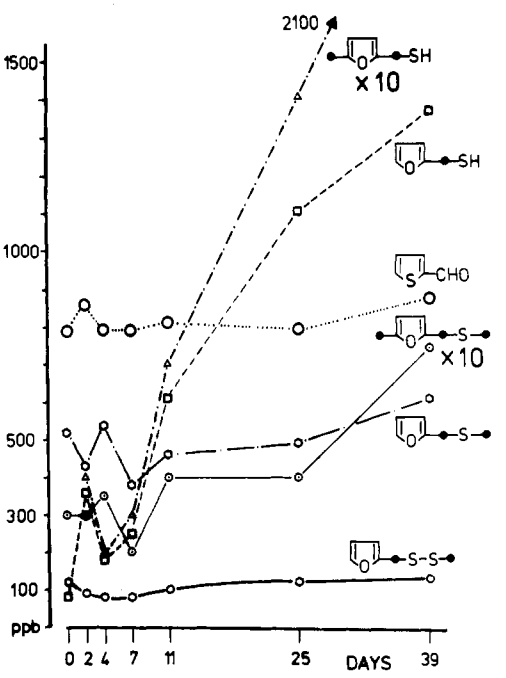

Figure 6. Changes of sulfur compounds during storage of roasted coffee beans.

furfuryl methyl sulfide, furfuryl methyl disulfide, and difurfuryl sulfide than Arabica coffees. On the other hand, Arabica coffees show higher amounts of kahweofuran and the sulfur-containing 5-methylfurfuryl components. The amounts of furfurylmercaptan and (5-methylfurfuryl)-mercaptan vary during aging of roasted coffee beans. This has been proven for Arabica, Robusta, and mixtures. High-grown Arabica coffee was medium roasted, packed with low air content, in a coffee roasting plant (Berlin), and stored at 25 °C. The amounts of sulfur components were determined periodically by GC–MS. Some results are shown in Figure 6. Fresh roasted coffee contains very low amounts of the mercaptans, but during storage they increase considerably. The concentrations of the corresponding sulfides and disulfides remain (nearly) constant. It is known that the aroma of fresh roasted coffee beans changes after a storage period of 10–14 days. This can be detected by expert panels or by headspace techniques (Vitzthum and Werkhoff, 1978). In our opinion furfurylmercaptan and (5-methylfurfuryl)mercaptan are responsible for these aroma changes.

The threshold of furfurylmercaptan in water was determined at 0.005 ppb by application of Teflon sniffing tubes and odorless water (Guadagni and Buttery, 1966). In concentrations of 0.01–0.5 ppb it was perceived like freshly roasted coffee; from 1 to 10 ppb it possessed the aroma of staled coffee with a sulfury note. Therefore, furfurylmercaptan may be considered as an impact component or off-flavor component depending on the concentration. The purified (5-methylfurfuryl)mercaptan had a threshold at 0.05 ppb, from 0.5 to 1 ppb it possessed a meaty aroma, and at higher concentrations it showed a sulfury mercaptan-like note. 2-Methyl-3-(methylthio)furan and 2-methyl-3-(methyldithio)furan showed thresholds in water at 0.05 and 0.01 ppb. In concentrations below 1 ppb, both constituents had a meaty aroma; at higher concentrations they delivered a thiamin-like note. The threshold of 2,5-dimethyl-3-(methyldithio)furan was determined at 0.01 ppb. At concentrations of 0.05–0.5 ppb it showed cooked meat like aroma; at higher concentrations it showed a thiamin-like note. Buttery et al. (1981) recently found an odor threshold of 4 parts of compound/10^{13} parts of water for the thiamin odor compound 1-methylbicyclo-[3.3.0]-2,4-dithia-8-oxaoctane. Furfuryl methyl disulfide is known as an impact component of white bread (Mulders et al., 1976) with a threshold of 0.04 ppb. Kahweofuran possessed in the pure state an intensive sulfury roasty odor quality as described by Ohloff and Flament (1978). The threshold in water was determined at 5 ppb. At concentrations of 10–100 ppb it was perceived as cooked meat with a slight coffee note. At higher concentrations it possessed a sulfury/roasty note.

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Multidetector Gas Chromatographic Determination and Confirmation of Airborne Triallate Residues in Saskatchewan

Raj Grover,* Lorne A. Kerr, and Shahamat U. Khan

Accumulative triallate samples were collected daily from May to November by using an air sampling train with polyurethane foam as the adsorbent material. A cleanup procedure was developed to improve the analysis of extracted triallate [*S*-(2,3,3-trichloroallyl) diisopropylthiocarbamate] by gas chromatography, using an electron capture (EC) detector and an alkali flame ionization detector (AFID). The limit of detection for airborne triallate was set at 0.5 ng m^{-3} (12.7 ng m^{-3} = 1 part per trillion triallate in the air). The maximum concentrations of triallate were found during the peak spraying season in May, being up to 200 ng m^{-3} in 1978 and 100 ng m^{-3} in 1979. The triallate concentrations in the air gradually decreased to 20 ng m^{-3} or less by midsummer, with some increase again in the fall, corresponding to the limited fall application of the chemical. After freeze up of the soil in early November, the triallate levels in the air fell below the detection limit. In general, the dramatic increases in triallate concentrations in the air during summer usually followed a rainfall event.

The presence of atmospheric residues of phenoxy herbicides, such as 2,4-D (2,4-dichlorophenoxyacetic acid), in the cereal growing regions of Canada and the United States is well documented (Farwell et al., 1976; Grover et al., 1976). It is also recognized that the major route of their input into the atmosphere is drift and vaporization losses during and immediately following their application (Grover et al., 1972, 1973). This short "release" period, combined with their relative nonpersistence in the environment (Loos, 1975), has no doubt limited the residence time of these herbicides in the atmospheric compartment to periods during or immediately after their application.

In contrast, however, the postapplication volatilization losses of soil-incorporated herbicides, such as trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine), to the atmospheric compartment may be a continuing process, extending over the entire growing season (White et al., 1977). Triallate, a soil-incorporated herbicide, with a vapor pressure similar to that of trifluralin (Grover et al., 1978), is used extensively in the Canadian prairies and the great plains of the United States to control wild oats (*Avena fatua* L.) in cereal and oilseed crops. The present study reports the levels and duration of triallate residues in the air in the Regina Plains, a high-use area.

MATERIALS AND METHODS

Location and Duration of Sampling. The field monitoring sites were at Regina in 1978 and 1979 and at Indian Head in 1979, both located in the cereal growing region of southern Saskatchewan. The sampling train was usually started in the first week of May each year and continued up to the freezing of the soil surface in early November to mid-November.

Sampling Procedure. Accumulative triallate samples were collected on 24-h basis on weekdays and 72-h basis on weekends by using polyurethane foam as the solid adsorbent. The sampling train consisted of (1) a glass tube with an inverted cone-shaped inlet set at 2 m from the ground, (2) an adsorbent chamber containing one or two, 45 mm diameter by 50 mm long, polyurethane foam plugs, (3) a calibrated flow meter (Gilmont Instruments, Inc., Great Neck, NY), and (4) an electric vacuum pump (Gelman Instrument Co., Ann Arbor, MI). The adsorbent chamber, flow meter, and pump were set in a Steven's screen weather box, to protect the system from sunlight, rain, etc. The air flow rate during sampling was set at 25 L min^{-1} with a needle valve and was checked during each foam plug change.

The adsorbent chamber contained only one foam plug in 1978. However, recovery studies indicated that two foam plugs in series were required to retain all of the entrapped triallate vapor, especially when weekend samples were run over the 72-h period at this high flow rate (Grover and Kerr, 1981). Consequently, two plugs in series were used in 1979 sampling. The exposed foam plugs for each sampling period were transferred to individual glass jars equipped with Teflon-lined screw-cap lids and the jars stored in a freezer until analysis.

Extraction, Cleanup, and Analysis. During 1978, the entrapped triallate vapor in each foam plug was Soxhlet extracted with 250 mL of *n*-hexane for 2 h. In 1979, when two plugs in series were used, the first plug was extracted with 300 mL of *n*-hexane for 2 h, after which it was replaced with the second plug and the extraction continued for another 2 h. The volume of the extracts was then reduced to ~1 mL by using a rotary evaporator.

Florisil (4 mL), deactivated with 5% water, was packed in a 7 mm i.d. glass column (Chromaflex No. 22, Kontes Glass Co., Vineland, NJ), containing *n*-hexane, and the excess hexane was drained slowly at the rate of 1 mL/min. The triallate residue was then quantitatively transferred to the column, by washing the extraction flask with five 2-mL portions of *n*-hexane, and the column eluted with 25 mL of 0.5% acetone in *n*-hexane. The first 10 mL of the eluate was discarded, the remaining eluate collected

Research Station, Agriculture Canada, Regina, Saskatchewan S4P 3A2, Canada (R.G. and L.A.K.), and Chemistry and Biology Research Institute, Agriculture Canada, Ottawa, Ontario K1A 0C6, Canada (S.U.K.).

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