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Note

Detection and identification of contaminants from foil-lined screw-cap sample vials

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The need to determine components of mixtures at the trace and ultra-trace levels requires procedures which avoid the introduction of contaminants. Contamination of samples may arise from several sources in sample preparation steps. The contamination of samples of trace organic compounds in an excess of solvent during concentration using various types of flexible plastic tubings has been noted and contact of solvents or samples with these materials must be rigorously avoided in procedures to avoid introduction of phthalate plasticizers[1].

Recently we observed that the chromatograms of trace amounts of organic compounds in a methanol solvent which were re-chromatographed after several weeks storage showed striking changes compared to the original chromatogram obtained under the same analytical conditions. Samples used in this study were obtained by methanol Soxhlet extraction of airborne particulate matter collected on glass fiber filters by high-volume filtration techniques[2,3]. These samples had been stored in glass sample vials with Sn–Pb alloy foil-lined screw caps at room temperature. Screw caps with metal foil liners are generally considered to be sufficiently inert to produce no sample contamination.

A study was conducted to determine the source and nature of the impurities found in our samples and it was concluded the contaminants originated from the cork backing of the metal foil apparently through permeation by the vapors of the methanol solvent. It was found that the contamination was eliminated by using a PTFL-lined cap liner over the metal foil.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard 5830A digital gas chromatograph equipped with a flame ionization detector (FID) and a Pyrex column (1.8 cm × 2 mm I.D.) packed with Aue Packing (AP)[4–7] (100–120 mesh) was used for the calculation of retention indices and rate of contamination. The gas chromatographic (GC) conditions were as follows:

helium flow-rate, 30 ml/min; injection port temperature, 240°; FID temperature, 300°; hydrogen flow-rate, 42 ml/min; air flow-rate, 250 ml/min; initial column temperature, 100° for 4 min; temperature program rate, 4°/min; final column temperature, 240° for 20 min; 3-μl injections.

Identification of contaminants was accomplished using the bench top Hewlett-Packard 5992A gas chromatograph–mass spectrometer calculator system equipped with a silicone membrane interface. The GC section of the gas chromatograph–mass spectrometer was equipped with another Pyrex column (1.8 m × 2 mm I.D.) packed with AP (100–120 mesh). The GC conditions used were: 1-μl injection; temperature program, as above; helium flow-rate, 25 ml/min; injector temperature, 240°; ion source temperature, 180°; transfer line temperature, 250°; ionizing voltage, 70 eV. The composition of the metal foil was found to be an Sn–Pb alloy (approx. 1:1) by using ion scattering spectrometry and secondary ion mass spectrometry data (3M-ISS/SIMS system).

Procedure

Two glass, 3.5-ml screw cap vials with screw caps lined with 0.005 in. metal foil (O.H. Johns Scientific, Toronto, Canada), were cleaned in an ultrasonic bath with a solution of Alconox detergent, followed by a rinsing with deionized, distilled water and methanol ("Distilled in Glass" grade; Burdick & Jackson, Musketon, Mich., U.S.A.).

One milliliter of methanol was dispensed into each vial. One vial was sealed using the regular foil-lined screw cap, the other vial was sealed by inserting a PTFE–rubber laminated disc (Pierce No. 12412; Chromatographic Specialties, Brockville, Canada) into the foil-lined screw cap with the PTFE side facing the solution. Both vials were inverted several times and left to stand at room temperature. Each methanol solution was analyzed by GC after 8 h, 1 day, 2 days and 3 days. The sample which indicated the most contamination after 3 days was analyzed by GC–MS to identify components.

A standard solution containing C_{14}–C_{34} *n*-alkanes was chromatographed each day prior to analysis of test samples. This is done routinely to check the performance of the analytical column and to provide retention time data for calculation of retention indices. The GC characteristics of the samples are displayed with the computer program GCPLOT which plots percentage total area of the individual peaks as a function of calculated retention index. The amount of contamination in the sample is displayed by the computer program PROFILE[8,9].

RESULTS AND DISCUSSION

GC analysis of the solutions after 8 h indicated the presence of three compounds in the vial with the regular screw cap. The vial with the PTFE–rubber disc insert indicated no contamination at this point. After 3 days, the vial with the regular foil-lined cap showed nine contaminants while the vial with the PTFE–rubber disc insert still indicated no contamination. A comparison of the data from the gas chromatograms for the contaminated samples is displayed by a composite GCPLOT in Fig. 1. The identification of each sample is given in the left-hand corner of the individual plot, and the total area response is indicated in the right-hand corner of the individual plots.
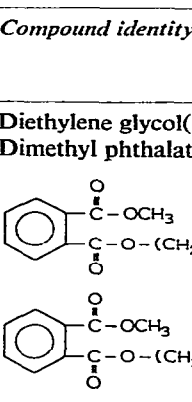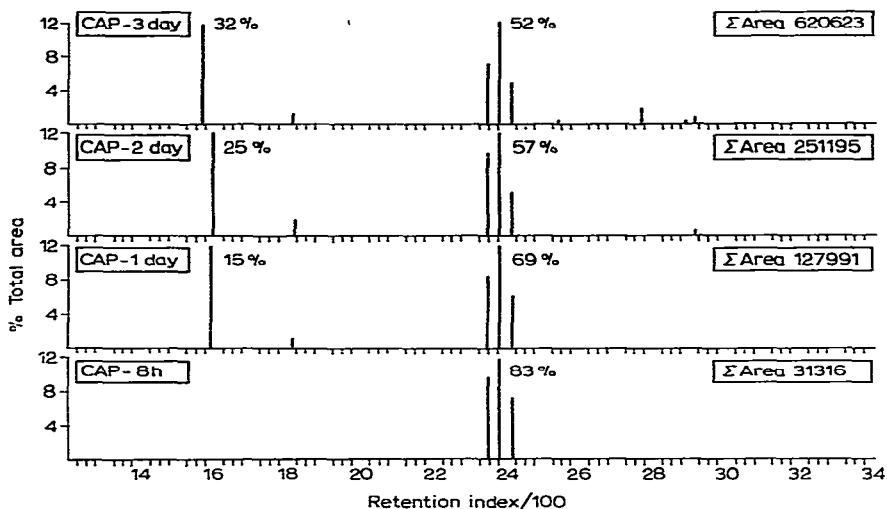
Fig. 1. GCPLOT of contaminated samples obtained after 8 h, 1 day, 2 days and 3 days. Peaks which exceed 12% are labelled.

TABLE I

ANALYTICAL RESULTS

Peak No.	Retention time (min)	Retention index	Mass spectrum no.*	Compound identity	Estimated concn. (10^{-6} g/ml)
1	5.6	1568	—	Diethylene glycol(10)	275
2	12.2	1816	—	Dimethyl phthalate(10)	9
3	24.3	2347	11	C_6H_4 with $C-OCH_3$ (O) and $C-O-(CH_2)_3-OCH_3$ (O)	60
4	25.1	2380	12	C_6H_4 with $C-OCH_3$ (O) and $C-O-(CH_2)_4-OCH_3$ (O)	445
5	25.8	2413	13	C_6H_4 with $C-OC_2H_5$ (O) and $C-O-(CH_2)_3-OC_2H_5$ (O)	42
6	28.3	2542	14	Unknown	2
7	32.4	2769	—	Benzyl butyl phthalate	6
8	34.4	2888	16	Unknown	2
9	34.7	2913	17	C_6H_4 with $C-OCH_3$ (O) and $C-O-(CH_2)_4-OC_3H_7$ (O)	5

* Mass spectra in Figs. 3 and 4 from which structures are postulated.

The total area response of the sample to the FID is an indication of the amount of organic material present. The total area response values shown in Fig. 1 were converted to representative concentrations using the response factor of dimethyl phthalate determined at the same analytical conditions. A response factor of 240 area
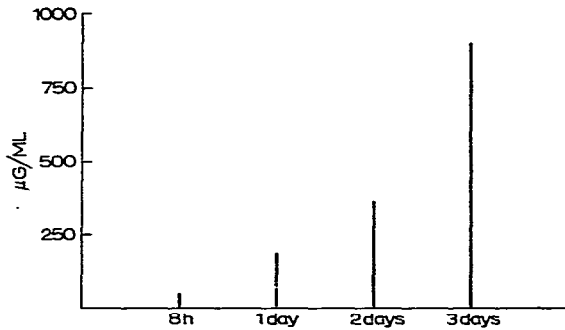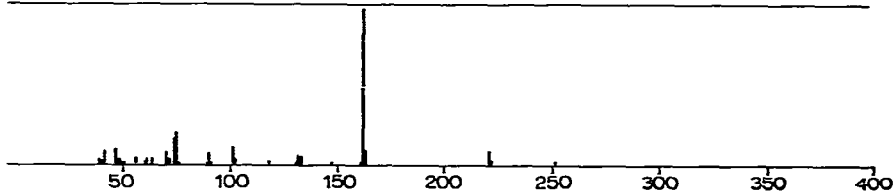

Fig. 2. PROFILE of contaminants observed with regular foil-lined screw cap.

Spectrum no 11   Sample no 54   Retention time = 24.3
File type = 2   Number of peaks detected = 60
Scanned from 40 to 400
Base peak = 163.0   Base peak abundance = 4768   Total abundance = 11685

Spectrum no 12   Sample no 54   Retention time = 25.1
File type = 2   Number of peaks detected = 102
Scanned from 40 to 400
Base peak = 163.0   Base peak abundance = 29056   Total abundance = 70056
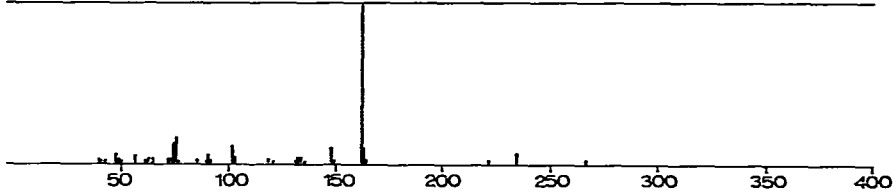
Spectrum no 13   Sample no 54   Retention time = 25.8
File type = 2   Number of peaks detected = 73
Scanned from 40 to 400
Base peak = 149.0   Base peak abundance = 1724   Total abundance = 6990
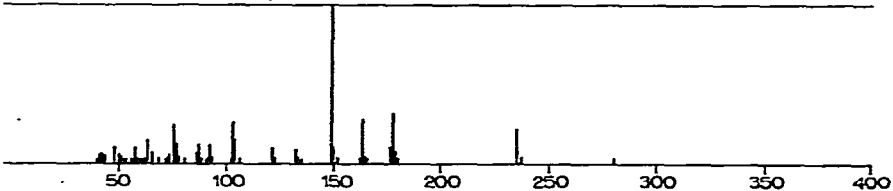

Fig. 3. Mass spectra of peaks 3, 4 and 5 listed in Table I.

counts per nanogram was used in the computer program PROFILE to produce Fig. 2 which indicates the total amount and the rate of contamination.

The identity of the individual contaminants was determined by GC–MS. Mass spectra of the individual components were obtained at 70 eV ionizing voltage for the mass range m/e 40–400. Interpretation of mass spectra was accomplished by comparison to reference compilations where available[10]. Where no reference mass spectra could be found which sufficiently matched the unknown spectra, identities were postulated by use of the usual mass spectral interpretation techniques[11].

The retention times, calculated retention indices and identities are given in Table I. Although no suitable reference spectra could be found for the compounds whose spectra appear in Figs. 3 and 4, a postulated structure is given for all these compounds with the exception of the two compounds present in very low amounts.

Since no contamination of the methanol was observed after 3 days when a PTFE–rubber laminated disc was inserted into the screw cap, and significant contamination is observed with the regular foil-lined screw cap, it is postulated that the

Spectrum no 14　　Sample no 54　　Retention time = 28.3
File type = 2　　Number of peaks detected = 36
Scanned from 40 to 400
Base peak = 163.0　　Base peak abundance = 153　　Total abundance = 540

Spectrum no 16　　Sample no 54　　Retention time = 34.4
File type = 2　　Number of peaks detected = 58
Scanned from 40 to 400
Base peak = 105.0　　Base peak abundance = 140　　Total abundance = 807

Spectrum no 17　　Sample no 54　　Retention time = 34.7
File type = 2　　Number of peaks detected = 55
Scanned from 40 to 400
Base peak = 105.0　　Base peak abundance = 322　　Total abundance = 1175
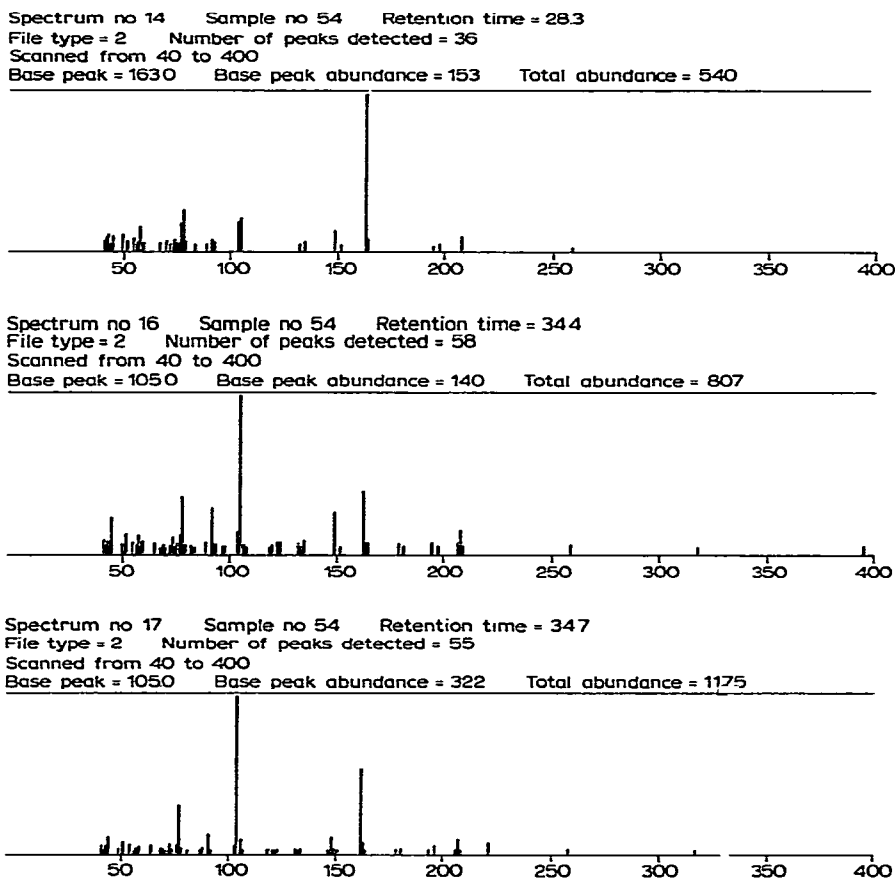

Fig. 4. Mass spectra of peaks 6, 8 and 9 listed in Table I..

contamination arises from the cork backing of the foil liner through permeation of the methanol vapors at room temperature. Solvents with different characteristics than methanol might produce a different degree of contamination. However, it is apparent that metal foil-lined vial caps of this type do permit contamination and PTFE-rubber laminated discs, or their equivalent, should be used in conjunction with screw cap vials to insure sample integrity.

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