Determination of Hexachloroacetone in Air

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Hexachloroacetone in air is collected in anhydrous methanol which reacts rapidly and quantitatively with hexachloroacetone. The reaction products, methyl trichloroacetate and chloroform, are determined by gas chromatography using an electron capture detector. The method can detect as little as 0.003 mg/m^3 hexachloroacetone in air. Moisture in air hydrolyzes hexachloroacetone to trichloroacetic acid and chloroform. The extent of hydrolysis can be calculated from the amounts of chloroform and methyl trichloroacetate found in methanol, if chloroform in air originates only from hydrolysis of hexachloroacetone. Unlike primary alcohols, secondary or tertiary alcohols do not react with hexachloroacetone.

Inhalation of air contaminated with hexachloroacetone (HCA) has produced pulmonary hemorrhage, edema, and congestion in rats (*1*). It is therefore necessary to monitor HCA in air at plant sites where HCA is produced or used.

This study revealed that the reactivity of HCA complicates the collection of its vapors for analysis. Sorption on solid adsorbents followed by thermal flash desorption and gas chromatography is unsatisfactory because of the reactions of HCA with the adsorbent or coadsorbed substances, e.g., water. Collection of HCA in an inert solvent suitable for gas chromatography, e.g., *n*-heptane, is not feasible either. When air is drawn through a solution of HCA in *n*-heptane, HCA disappears while chloroform is formed and extraneous peaks appear in the gas chromatogram (Figure 1). HCA reacts with the moisture in air producing chloroform and trichloroacetic acid (*2, 3*)

$$CCl_3COCCl_3 + H_2O \rightarrow CCl_3COOH + CHCl_3$$

Hydrolysis of the C–Cl bond is less than 2% of the reaction producing trichloroacetic acid (*2*). The extraneous peaks observed in the gas chromatogram are probably secondary peaks originating from trichloroacetic acid.

The problems of collecting HCA per se were resolved in this study by absorbing HCA in a reagent that converts HCA rapidly to a stable derivative suitable for gas chromatography. Kulka (*4*) reported that HCA forms chloroform and ethyl trichloroacetate when heated in ethanol with a small amount of aluminum ethoxide. The present author found that heating with a catalyst is unnecessary since primary alcohols, RH_2OH, react rapidly with HCA and form the corresponding alkyl ester of trichloroacetic acid and chloroform

$$CCl_3COCCl_3 + RCH_2OH \rightarrow CCl_3COOCH_2R + CHCl_3$$

Gas chromatography of HCA solutions in alcohol indicates that secondary alcohols (2-propanol and 2(2*H*)-hexafluoropropanol were tested) and tertiary alcohol (*tert*-butyl alcohol) do not react with HCA in a similar manner.

The retention times of trichloroacetic acid esters of primary alcohols increase in the order: methyl ester, 9.7 min; ethyl ester, 11.2 min; and *n*-butyl ester, 15.0 min. The retention times of alcohols increase in the same order with the result that chloroform, the other solvolysis product, can be separated conveniently only from methanol. We selected therefore methanol for the reactive sorption of HCA.

EXPERIMENTAL SECTION

Reagents and Materials. Hexachloroacetone, purified by distillation, was obtained from du Pont de Nemours & Co., Inc. (Wilmington, DE).

Methanol and chloroform were purchased from Burdick & Jackson Laboratories, Inc. (Muskegon, MI), ethanol (pure ethyl alcohol, dehydrated, U.S.P.) from U.S. Industrial Chemicals Co., the glass column for chromatography and packing (5% Dexsil 300 on 80/100 Chromosorb G, HP) from Supelco, Inc. (Bellefonte, PA), and compressed air and nitrogen from Liquid Carbonic Corp. (Chicago, IL). Air and nitrogen were dried by passing through Lab-Mate Gas Filter Driers purchased from Mann-Made Enterprises, Inc. (Maddison, IL).

Sampling Procedure. The apparatus for collecting HCA consisted of three midget impingers connected in series (Figure 2). The impingers were dried and 10 mL of anhydrous methanol was added to each impinger. The first impinger was kept at ambient temperature to prevent moisture from condensing in the lines. The two impingers following the first impinger were placed into a container made of Styrofoam and cooled in dry ice to capture chloroform and to reduce evaporation of methanol in the air stream. The train of the impingers was connected to a pump (Model 222-3, SKC, Inc., Eighty Four, PA) via a tube containing charcoal to prevent solvent vapor from the impingers entering the pump. The pumping rate was usually 140 mL/min. The contents of the first two impingers were combined and 4 mL of the internal standard (0.30 g/L of 1,2-dichloroethane in methanol) was added. Two milliliters of the internal standard were added to the last (third) impinger. The solutions were analyzed by gas chromatography.

No methyl trichloroacetate, a reaction product of HCA with methanol, was detected in the third impinger. Solvent carry-over from a cooled impinger during air sampling was negligible.

Gas Chromatography. A Varian 3700 gas chromatograph was equipped with an electron capture detector and a column (6 ft long, $^1/_4$ in. o.d., 2 mm i.d.) packed with 5% Dexsil 300 on 80/100 Chromosorb G, HP. The flow rate of 90% argon–10% methane carrier gas was 30 mL/min. A 5-μL sample was injected on column and the chromatograph programmed from 40 to 250 °C at 8 °C/min with a 2-min initial hold. The detector temperature was 300 °C.

The injection of samples was alternated with the injection of pure solvent to maintain a clean base line and recondition the column.

To rule out possible interference by an air contaminant having the same retention time as the internal standard, a sample of the analyte in the impinger was injected into the gas chromatograph before adding the internal standard. The internal standard was added when no extraneous peaks were detected in the area of interest. Alternatively, the internal standard was added to pure methanol, injected alternately with the analyte, and used as an external standard.

A Hewlett-Packard computer, Model 3354, was used to calculate peak areas.

HCA Recovery. The cell used to vaporize HCA (Figure 3) consisted of a 10-mL spetum vial, equipped with a syringe, an air inlet tube, and an outlet tube, both made of Teflon. The outlet tube was connected to a 20 cm long $^1/_8$ in o.d. Teflon tubing attached to the inlet of the impingers, shown in Figure 2.

A solution of HCA in *n*-heptane was added by means of the syringe in small droplets gradually over a period of several hours, and pumping continued for 1 h after the last addition was made. At the completion of the recovery test 5 mL of absolute methanol

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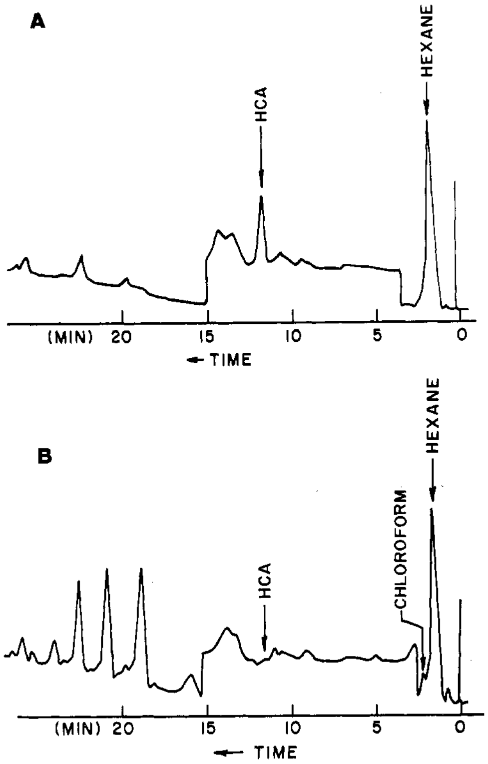

Figure 1. Disappearance of hexachloroacetone in the impinger during air sampling: (A) before sampling, (B) after sampling; attenuation 320, except for attenuation 80 during the 4-min to 15-min period.

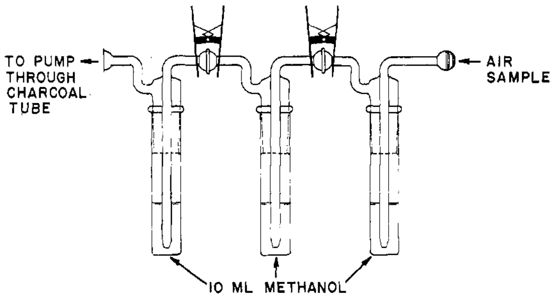

Figure 2. Apparatus for collecting HCA in air.

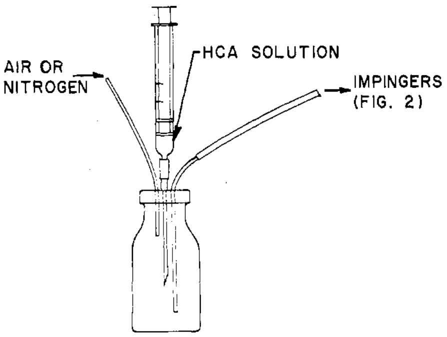

Figure 3. Evaporation cell.

was injected into the vial and analyzed for methyl trichloroacetate to verify complete evaporation of HCA.

The amount of HCA evaporated was determined by weighing the syringe at the start and at the end of the recovery test. The syringes used for this purpose were 50-μL and 250-μL Hamilton 1000 Series gastight fixed needle syringes (Supelco, Inc.) and 0.5-mL Glaspak syringes (Becton & Dickinson Co., Rutherford, NJ). The syringes were tested for vapor leaks by drawing hexane into the syringe, inserting the needle into a septum vial, weighing the assembly after 2 and 4 h, injecting half of the hexane into the septum vial, and reweighing the assembly 3 h later. No weight loss was observed.

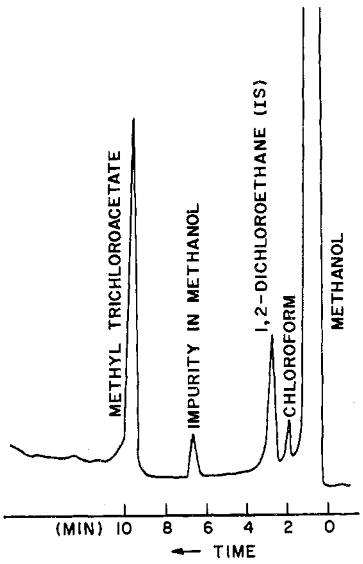

Figure 4. Gas chromatogram of methanol used to collect hexachloroacetone in plant air.

RESULTS AND DISCUSSION

Gas Chromatography of HCA Reacted with Methanol. The reaction of HCA with methanol produces methyl trichloroacetate (MTA) and chloroform

$$CCl_3COCCl_3 + CH_3OH \rightarrow CCl_3COOCH_3 + CHCl_3$$

MTA and chloroform both can be separated from the solvent and determined by gas chromatography (Figure 4). The reaction of HCA with methanol is rapid, even when HCA is added to methanol cooled in dry ice and a sample of the reaction mixture injected immediately into the gas chromatograph. The amount of HCA, determined immediately after adding 1.3 g of HCA to cold methanol, is 98–99% of the value obtained by injecting a sample 2–24 h later into the gas chromatograph.

A calibration curve of HCA, converted in methanol to chloroform and the methyl trichloroacetate, was prepared with 1,2-dichloroethane as the internal standard. The amount of HCA in micrograms was calculated as

$$W_{HCA} = (A_{MTA}/A_{IS} - 0.00135)0.00335W_{IS}$$

where A_{MTA} and A_{IS} are the areas and W_{HCA} and W_{IS} the weights of HCA and the internal standard, respectively, in micrograms.

The linear correlation was found to be 0.999 999 8 (five points).

Calibration of the gas chromatograph with chloroform and 1,2-dichloroethane (internal standard) gave the following relationship (linear correlation 0.999 99 of four points)

$$W_{CHCl_3} = (A_{CHCl_3}/A_{IS} - 0.00296)0.00800W_{IS}$$

The amount of chloroform found in methanol after adding HCA is close to the theoretical amount of 1 mol per 1 mol HCA.

HCA taken, μg	chloroform found, μg	mole ratio chloroform/ HCA
0.215	0.088	0.91
2.149	0.95	0.98
10.74	4.55	0.94

Hydrolysis of HCA by Water Vapor in Air. Since HCA is trapped in methanol together with water absorbed from air, the effect of water on the conversion of HCA to MTA had to

Table I. Recovery of HCA

atmospheric condition	volume of air pumped, L	recovery of HCA, %	recovery of $CHCl_3$, %	$CHCl_3$/MTA mole ratio
medium humidity (40% rel)	9.8	65	93	1.4
humid (70% rel humidity)	11.7	33	100	3.0
humid air drawn through a drier into the HCA cell connected to the air sampler	14.3	87	100	1.1
methyl trichloroacetate evaporated instead of hexachloroacetone, by drawing humid air through the cell	11.2	101		

Table II. Recovery of Hexachloroacetone (HCA) in Air

analysis no.	alcohol in impinger	amt of HCA vaporized, µg	vol of air pumped, L	pumping time, h	% HCA recovered as CCl_3COOR[b]	atmospheric conditions		
						temp, °C	humidity, %	mg of H_2O/L in air
1	ethanol[a]	1.06	40.1	5.0	32	25	67	15.5
2		1.02	40.0	5.2	75	23	41	8.5
3		20.7	41.1	5.0	56	25	67	15.5
4		19.8	36.0	4.8	59	25	67	15.5
5		20.3	34.2	4.3	90	compressed air		
6		19.4	33.7	4.3	98	dry nitrogen		
7	methanol[a]	0.99	41.2	5.2	88	23	41	8.5
8		3.88	33.9	4.3	82	23	41	8.5
9		4.02	40.9	5.2	82	22	40	7.8
10		9.80	32.6	4.3	96	23	41	8.5
11		20.6	35.1	4.8	87	25	67	15.5

[a] Runs 4 and 11, also 2 and 7, were made simultaneously with two identical air samplers side by side. [b] R is CH_3 or C_2H_5.

Table III. Hexachloroacetone and Chloroform in Air

analysis no.	sampling conditions		found			atmospheric conditions		
				$CHCl_3$				
	time	vol, L	amt of HCA, mg/m^3	µg in impingers	mg/m^3 in air	temp, °C	humidity, %	g of H_2O/m^3
1	5 h 35 min	41.4	0.003	0.189	0.189			
2	5 h 32 min	41.9	0.14	7.22	0.109			
3	5 h	38.8	0.045	4.27	0.089	20.4	38	6.73
4	5 h 30 min	39.0	0.006	0.38	0.072	20.0	40	6.92
5	5 h	33.2	0.029	5.29	0.146	19.5	47	7.90
6	5 h	35.3	0.047	0.098	0.003	18.0	45	6.91
7	1 h 7 min	9.1	0.25	1.28	0.028	14.5	60.5	7.52
8	1 h 7 min	9.9	0.28	1.68	0.044	14.5	60.5	7.52
9	1 h	8.0	0.14	0.66	0.020	25.1	41.1	9.53

be determined. The results suggest that the reaction rate of water with HCA is of the same magnitude as that of methanol with HCA. When a known amount (0.69 to 0.71 µg) of HCA is added to 10 mL of methanol containing 0.20 g of water (mole ratio 22:1), the conversion of HCA to MTA drops to 92%. When the water concentration is increased to 0.50 g in 10 mL of methanol, conversion of HCA to MTA drops to 87%. Assuming 80% humidity and 27 °C temperature, 10 L and 25 L of air contain 0.20 g and 0.50 g of water, respectively. Consequently, significant losses of HCA absorbed in methanol can be expected when sampling humid air, but the actual losses should be smaller than the results above suggest. Methanol is anhydrous at the start of sampling and only at the end of sampling has its water content increased to the levels illustrated with the examples above. MTA is stable in moist methanol. In solutions described above, the loss of MTA was about 3% relative in 4 h at ambient temperature. Trichloroacetic acid (TCA), a hydrolysis product of HCA, does not react with methanol at ambient temperature; 99.1% of trichloroacetic acid was found to be present after a 5.1 M solution of TCA in methanol was allowed to stand for 1 h and titrated with 0.01 N NaOH. After 7 h, 94% of the acid was still present. Consequently, MTA in methanol represents unhydrolyzed HCA.

Although HCA trapped in methanol is converted nearly quantitatively to MTA, a substantial portion of HCA may hydrolyze in moist air before reaching the air sampler. A complete recovery of HCA introduced into air is therefore unlikely. This is illustrated with recovery data in Table I. HCA (1.20 µg) dissolved in 0.50 mL of *n*-heptane was placed into a vessel (Figure 3) through which air was drawn into the air sampler (Figure 2). The complete evaporation of HCA was confirmed by washing the vessel with methanol and using gas chromatography.

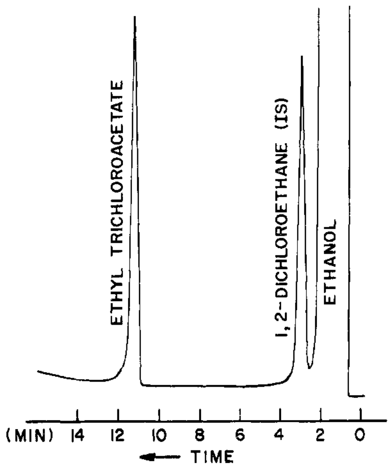

Figure 5. Gas chromatogram of hexachloroacetone converted to ethyl trichloroacetate in ethanol.

Although the recovery of HCA depended on humidity, chloroform was found in expected amounts. The reactions of HCA with methanol and water both produce chloroform

$$CCl_3COCCl_3 + CH_3OH \rightarrow CCl_3COOCH_3 + CHCl_3$$

$$CCl_3COCCl_3 + H_2O \rightarrow CCl_3COOH + CHCl_3$$

The mole ratio of $CHCl_3$ to MTA found in methanol indicates the extent of hydrolysis if chloroform present in air does not originate from other sources. This is important because the hydrolysis products of HCA have also low exposure limits; trichloroacetic acid has a TWA of 5 mg/m^3 and chloroform has a TWA of 50 mg/m^3 (*5*).

Determination of HCA as Ethyl Trichloroacetate. Palomaa, Salmi, and Korte have reported (*6*) that ethyl trichloroacetate is more stable to hydrolysis than methyl trichloroacetate. The efficacies of ethanol and methanol in absorbing HCA from air were therefore compared (Table II). The higher yield of HCA conversion in methanol than in ethanol suggests that hydrolysis of the alkyl trichloroacetate formed in alcohol is not a significant factor. The conversion of HCA to an alkyl trichloroacetate depends on hydrolysis of HCA by water in air and in alcohol, and consequently on the reaction rate of HCA with alcohol relative to that with water. The reaction of HCA with ethanol was not investigated further, because the use of ethanol as the sorbent had no apparent advantages, but the disadvantage of difficult separation of chloroform by gas chromatography (Figure 5).

HCA in Air. Analysis of air sampled with methanol as the sorbent at the site of HCA production is illustrated in Table III. The precision of sampling is shown with samples 7 and 8, simultaneously obtained by two air samplers positioned 2 m apart. The amounts of HCA found in air were 0.25 and 0.28 mg/m^3, the amounts of chloroform in air were 0.03 and 0.04 mg/m^3 (this is the amount of chloroform found in methanol less the amount of chloroform corresponding to the amount of MTA found).

A method for the determination of traces of trichloroacetic acid in air remains to be developed. However, the highest possible concentration of trichloroacetic acid formed by hydrolysis of HCA in air can be calculated from the chloroform concentration in air. In samples 7 and 8 (Table III) the trichloroacetic acid concentrations resulting from HCA hydrolysis were 0.04 and 0.06 mg/m^3, respectively, or less.

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Registry No. Hexachloroacetone, 116-16-5; methanol, 67-56-1.

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