Determination of Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Various Materials

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Introduction

The determination of specific chlorinated dibenzo-p-dioxins is complicated by the large number of structurally similar compounds which are normally present in many samples as well as the usual problems of removal of the matrix itself. Thus separation techniques with the highest resolving power and detectors with the most specific response must be used. The certainty of the results must be established so that proper action can be taken to prevent exposure by plant personnel and to assure that these materials are not spread in the environment. In order properly to assess the wide range of biological activity which these compounds exhibit, the final determination must be specific, sensitive, and reliable.

The search for such a method began at Dow Chemical Company in 1964 when the caustic insoluble residue from 2,4,5-trichlorophenol distillation residue was examined by thin-layer chromatography and the most biologically active spot identified as 2,3,7,8-tetrachlorodibenzo-p-dioxin by comparison with synthesized material (N. E. Skelly, Dow Chemical Company, personal communication, 1964). The isolated and synthesized materials were compared and examined by mass spectrometry, infrared spectrometry, gas chromatography, and elemental analysis. Later, unequivocal proof of structure was established by single-crystal x-ray spectrometry (1). Mass spectral data were taken directly from the same crystal (J. Tou, Dow Chemical Company, personal communication, 1973). Reference has been made to this original material when new material was synthesized (2), when labeled compounds were prepared (3), or when new methods were examined for the isolation or separation and determination of this material. Similar procedures were employed for proof of structure of 2,7-dichlorodibenzo-p-dioxin (4) and octachlorodibenzo-p-dioxin (5). Mass spectral patterns of each material were determined as well. Other techniques used to examine these materials include ultraviolet spectrometry, gas chromatography, and elemental analysis (where the amounts of material were sufficient).

Experimental

Determination of Purity of Standards.

The purity of any synthesized material or compounds used as standards was determined by gas chromatography and/or mass spectrometry. Solid probe introduction of samples into a Varian MAT CH4 mass spectrometer and monitoring the molecular ion regions for the presence of lower or higher

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chlorinated compounds proved to be the most sensitive method for the determination of impurities. Although this technique was not developed for final analysis, by careful manipulation of the sample size and probe introduction conditions semiquantitative determinations (±25% relative error) could be made down to about 50 ppm (L. Shadoff and J. Tou, Dow Chemical Company, personal communication, 1969).

After examination of a number of different gas-liquid chromatographic conditions, most examinations of synthesized or isolated compounds for the determination of impurities were made on a trifluoropropylmethyl silicone fluid stationary phase: QF–1 or OV–210 (H. Gill and R. Solomon, Method MLW. 65.10, The Dow Chemical Company, 1965). Although this stationary phase gives good resolution of isomers, it does not have the requisite thermal stability for long-term operation. An acceptable substitute was found to be SE–30 or OV–17.

Several other techniques were investigated for the determination of purity of synthesized or isolated materials. Although differential scanning calorimetry has been employed (6) for a variety of pesticides and herbicides, the degree of purity obtained by this method was not consistent with mass spectrometry or gas–liquid chromatography (R. Hummel, The Dow Chemical Company, personal communication, 1970).

Gas chromatography was used to determine the solubility of 2,3,7,8-tetrachlorodibenzo-p-dioxin in a variety of solvents. Table 1 shows the solubility and physical properties of material synthesized in our laboratories.

Preparation of Reagents

Dowex 21K anion-exchange resin (hydroxide form) was obtained from The Dow Chemical Company, Midland, Michigan, as the chloride form, 80/100 mesh. It was washed well with methanol and water and converted to the hydroxide form by passing a 5% solution of sodium hydroxide through a 1 m × 5 cm column of resin. After washing well with water and finally with meth-

Table. 1: Composition and physical properties of 2,3,7,8-tetrachlorodibenzo-p-dioxin.[a]

	Found	Theory
Composition		
Carbon, %	45.0	44.7
Hydrogen, %	1.34	1.25
Chlorine, %	42.7	44.0
Molecular weight	319	322
Melting point, °C	303–305	
Solubility in various solvents, g/100g		
o-Dichlorobenzene	0.14	
Chlorobenzene	0.072	
Benzene	0.057	
Chloroform	0.037	
Acetone	0.011	
n-Octanol	0.0048	
Methanol	0.001	
Orange Herbicide	0.058	
Water	0.2×10^{-7} (0.2 ppb)	

[a] Data from N. E. Skelly, G. Kallos, and L. Shadoff, Dow Chemical Company, personal communication.

anol, 500-ml portions were transferred to 1-liter bottles, the excess methanol decanted off, and 500 ml benzene added and the contents mixed well. These bottles were stored in a refrigerator to retard decomposition.

Dowex MR-3 mixed-bed ion-exchange resin (hydrogen and hydroxide form) was also obtained internally. After washing with water and methanol, it was rinsed in a 1 m × 5 cm column with 4 1. methanol and stored in 1:1 (v/v) benzene–methanol as before.

Silica gel (high purity, 100–200 mesh, Curtin Scientific Co., Midland) was used as received. Columns were prepared by pouring slowly with stirring 50 g of silica gel into 100 ml of 20% (v/v) benzene in hexane. The slurry was transferred to a 75 × 1.9 cm chromatographic column with Teflon stopcock and glass wool plug at the bottom. The bed was tapped gently to settle the silica and the stopcock opened to allow the liquid to drain to the top of the bed. After washing with an additional 100 ml of 20% benzene in hexane, the columns were ready for use.

Gas chromatography columns were prepared by the slow addition of column packing with gentle tapping or vibration under vacuum from the outlet. Stationary phase concentrations of 3% (w/w) were used throughout this work and all columns were 2.5–3.5 mm ID glass tubing. Some columns required on-column silylation (Sylon BTZ, Supelco Co., Bellefonte, Pa.) to reduce tailing of octachlorodibenzo-p-dioxin.

Standard solutions were prepared by weight from the appropriate materials to give 100–500 ppm solutions in benzene. All solvents used for standard solutions were "distilled-in-glass" quality (Burdick and Jackson, Muskegon, Mi.). Standard solutions were transferred to polyethylene-capped vials and stored in a freezer prior to dilution and use.

Gas-chromatographic determinations of 2,3,7,8-tetrachlorodibenzo-p-dioxin were performed by using GLC with flame ionization detection on the neutral residue from a sample. Dow methods MLW.65.10 and 65.11 use 50 to 100 g samples and contain the residue in about 1 ml of solution. An alternate method (CIPAC method) uses a 25 g sample, with sample cleanup by extraction, column chromatography, and thin-layer chromatography and detection by GLC with electron-capture detection.

Procedure for GC-MS Determination of Chlorinated Dioxins

The matrix was separated from the neutral components by one of the following procedures.

2,4,5-Trichlorophenol—A 50-g portion of sample was weighed into a 500-ml bottle, and 60 ml of aqueous sodium hydroxide and 20 ml of benzene were added. Vigorous extraction was carried out for 5 min. The layers were allowed to separate, the benzene decanted and evaporated under a gentle stream of dry, filtered air at room temperature, with removal as soon as the last visible solvent had evaporated. A 1-ml portion of chloroform was added and 2 μl of this solution was injected into the gas chromatograph. The height of the peak at the retention time of 2,3,7,8-tetrachlorodibenzo-p-dioxin was compared with that of a standard.

2,4,5-Trichlorophenoxyacetic acid, pentachlorophenol—A 5.0-g sample was weighed into a 30-ml beaker and dissolved in 20 ml 1:1 (v/v) benzene–methanol. The solution was transferred quantitatively with 10 ml washing to the top of a 50-cm × 2-cm column of Dowex 21K hydroxide-form ion-exchange resin, and the liquid level was allowed to fall to the top of the bed. A 125-ml portion of solvent was added and the column effluent collected. The effluent was concentrated as described for trichlorophenol.

Sodium pentachlorophenate—A 5.0-g portion of sample was weighed and dissolved in 25 ml 1:1 (v/v) benzene–methanol. This was transferred quantitatively to a 50-cm ×2-cm column of Dowex MR-3 resin. Elution, concentration, and identification were as described above.

Esters of 2,4,5-T acid, formulations, and nonionizable samples (fats, oils, natural product extracts)—A 5.0-g sample or its equivalent was weighed, dissolved in 25 ml 20% (v/v) benzene in hexane, and transferred quantitatively to the top of a 50 × 2 cm column of silica gel in the same solvent. The procedure was as detailed for 2,4,5-trichlorophenoxyacetic acid, except that 20% benzene is used in place of 1:1 benzene–methanol.

Gas Chromatography—Mass Spectrometry Operating Conditions

The instrument used was a LKB 9000, with MID accessory.

GC conditions were as follows: Column, 3% OV–210 on 80/100 Chromosorb W–HP or 3% SE–30 on 90/100 Anakrom ABS; GC inlet temperature, 235° C; GC column temperature, 200–230° C; flow, 40 cc/min He; sample size, 2μl injected. MS conditions were as follows: separator temperature, 250° C; ion source temperature, 270° C; ionization potential, 70 eV; emission current, 60μA; accelerating voltage, 3.5 kV; multiplier voltage, 3.3 kV (80% of maximum); nominal resolution, ~600 (10% valley); MID frequency, 0.5 sec/

ion; MID ions, M, M+2, M+4; recorder, 50–500–5000 mV oscillograph.

Quantitation was achieved by direct measurement of peak height of each isotope ion and comparison with standards. Where isomers were not completely resolved, peak area measurements were made using digital computor integration of the signal. Care was taken to always inject the same volume of solution and standards were run frequently to check reproducibility and linearity. Whenever possible, standards were run to "bracket" the concentrations observed in samples.

Liquid-Liquid Column Chromatographic Determination of Chlorinated Dibenzo-p-Dioxins

Liquid–liquid column chromatography was performed by using the reversed-phase mode of operation. Separations were achieved using a bonded stationary phase prepared in our laboratories (7). Although this material was considerably more retentive than other materials available, use was also made of two commercial octadecyl-coated silica packings: ODS Permaphase (E. I. du Pont, Wilmington, Del.) and C_{18}-Corasil (Waters Associates, Framingham, Mass.). Both materials proved acceptable, with the limits of application of this method as discussed later. Early work was performed on a variable-wavelength liquid chromatograph constructed in our laboratory (8). Recent work was carried out on the du Pont model 820, with 254 nm ultraviolet detector with only a slight decrease in sensitivity. Specific operating conditions are noted on Figures 1 and 4.

Results and Discussion

As previously mentioned, the requirements of selectivity and sensitivity dictated that careful attention be paid to sample cleanup procedures for those measurement systems which employ nonselective detectors GLC–FID, GLC–EC). Several workers have previously noted the difficulty in achieving adequate cleanup to ensure accurate results without loss of chlorinated

dibenzo-p-dioxins (9–12). Early work in our laboratory (R. Solomon et al. Dow Chemical Company, personal communication, 1968) showed that the use of a simple extraction from alkaline solution was accurate for 2,4,5-trichlorophenol down to 0.5 ppm. The use of a method developed by several laboratories for the Collaborative International Pesticides Advisory Committee (CIPAC) which employed a more extensive and time-consuming liquid chromatographic cleanup permitted a comparison of methods for 2,4,5-trichlorophenol (2,4,5-TCP) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T acid) (13). Table 2 indicates the results of the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in 2,4,5-TCP and 2,4,5-T acid by these three methods. As can be seen, the recovery of added 2,3,7,8-dioxin is excellent for these types of samples. When an attempt was made to analyze esters of 2,4,5-T acid by these methods, many interfering peaks were observed in the resulting chromatograms and no accurate results could be obtained. As a result, any determinations of 2,3,7,8-dioxin in these materials could only be considered maximum values unless confirmed by some alternate method.

Table 2. Determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin by gas chromatography.

	2,3,7,8-Dioxin, ppm		
Sample	Added	Found	Method
2,4,5-Trichlorophenol	0.0	1.6	Dow MLW
	2.2	3.8	65.10 [a]
	4.6	6.5	
2,4,5-T Acid	0.0	<0.5	Dow MLW
	1.6	1.4	65.11 [a]
	1.9	1.8	
	3.8	4.1	
2,4,5-T Acid	0.00	<0.01	CIPAC
	0.043	0.05	Method [b]
	0.086	0.09	
	0.43	0.42	

[a] Methods uses 50–100 g samples, 100-fold concentration by extraction, and flame-ionization detection.
[b] Method uses 10–25 g samples, LC plus TLC cleanup, and electron-capture detection.

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The use of liquid–liquid column chromatography offers some potential for more selective determinations by virtue of monitoring the ultraviolet absorption at the λ_{max} of the compound of interest (305 nm for 2,3,7,8-dioxin). When this method was applied to a 1-g sample of material used by Bionetics Research Laboratory in a teratology study (14), the results shown in Figure 1 were obtained. The concentration of 2,3,7,8-dioxin in this sample was confirmed by gas–liquid chromatography by Dow method 65.11.
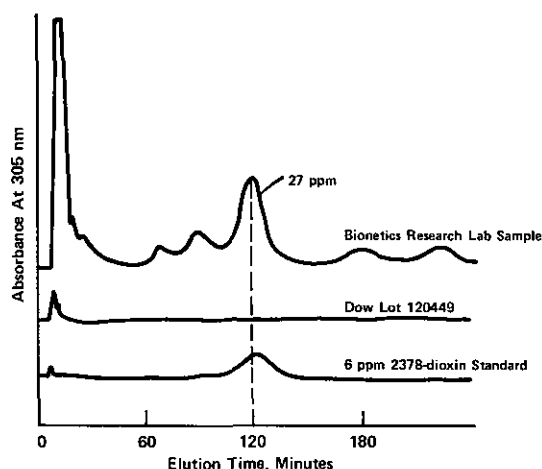
FIGURE 1. Liquid–liquid column chromatographic determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Conditions: column, BrC$_{18}$ Porasil; 500 × 2 mm; solvent, 20% H$_2$O in C$_2$H$_5$OH; Flow rate, 1 ml/min; sensitivity, 0.1 absolute unit, full scale; sample, 5 μl of 10X concentration of alkaline extract of 2,4,5-T acid.

The use of gas–liquid chromatography in combination with mass spectrometry (GC–MS) offers significant potential for selective determination of particular components in complex mixtures (15, 16). Figure 2 shows the schematic diagram of the GC–MS which uses the Becker-Ryhage double molecular jet separator. An accessory used in conjunction with the basic instrument provides for repetitively incrementing the accelerating voltage over a narrow range to alternately focus three different mass ions on the detector.

This mode of operation, termed multiple ion detection (MID), permits selective and sensitive determination by virtue of simultaneously requiring for detection that the sample have (a) a component with chromatographic retention time identical to the compound of interest; (b) ions at a mass identical to the compound of interest; (c) ions with the same intensity relative to each other as the compound of interest.

The coincident occurrence of all three factors permits a relatively high degree of assurance that the compound of interest is indeed present and also permits relatively accurate measurement of the concentration. When combined with the possibility of concentrating the sample by selective removal of the matrix, detection limits well below 1 ppm in the original sample are possible. When this spectrometer is operated close to maximum sensitivity, detection limits of 6×10^{-12} g (6 pg) with an approximate 10/1 signal/noise ratio are obtained as shown in Figure 3. As can be seen, the M, M+2, and M+4 ions retain the relative intensity ratios expected for a compound with four chlorine atoms (0.75:1.00:0.50).

With the advantages of detector selectivity, sample cleanup methods can be selected which emphasize difference between the compound of interest and the matrix, rather than requiring physical separation of individual minor components.

This permits high concentration factors to be achieved as well as avoids losses of the compound of interest which accompany multistep or harsh "cleanup" procedures. Table 3 outlines the various sample cleanup procedures which we have used for examination of a variety of samples for various chlorinated dibenzo-*p*-dioxins.

When these methods are applied to the determination of 2,3,7,8-dioxin in low residue samples, the agreement between this method (GC–MS) and the previously used GLC methods is very good. Table 4 lists the comparative data for one sample of 2,4,5-T acid, to which had been added known amounts of 2,3,7,8-dioxin and analyzed collaboratively by a number of different labora-
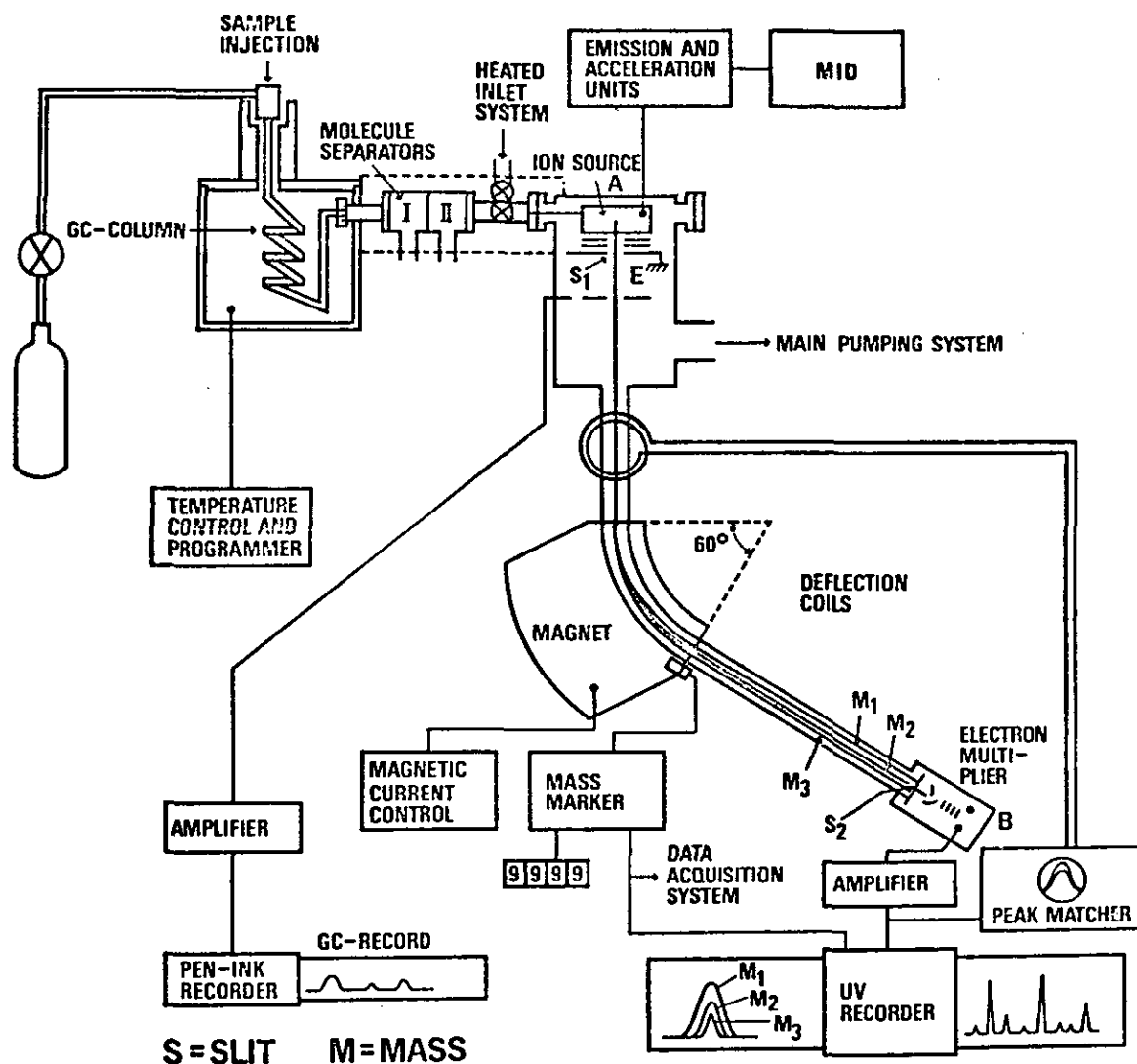
FIGURE 2. Schematic diagram of LKB 9000 gas chromatograph—mass spectrometer.

tories including the Dow Chemical Company. The results shown are the pooled results of 11 laboratories compared to duplicate determinations in our laboratory by the GC–MS method (E. Wilke, Dow Chemical Company, personal communication, 1971). Additional results are given showing the excellent agreement between GC–MS and the conventional GLC method (Dow MLW.65.10 and Dow 65.11) for 2,4,5-TCP and 2,4,5-T acid.

The accuracy of this GC–MS method for a wide variety of chlorophenolic compounds is shown in Table 5. Again as can be seen, the recovery is excellent, down to the detection limit of 0.05 ppm.

These methods have also been applied to the determination of 2,3,7,8-dioxin in beef fat to which had been added various trichlorinated compounds and subjected to conditions equivalent to cooking for various periods of time (R. Hummel, Dow Chemical Company, personal communication, 1970). Table 6 illustrates that no 2,3,7,8-dioxin was detected under any of these rather severe conditions.
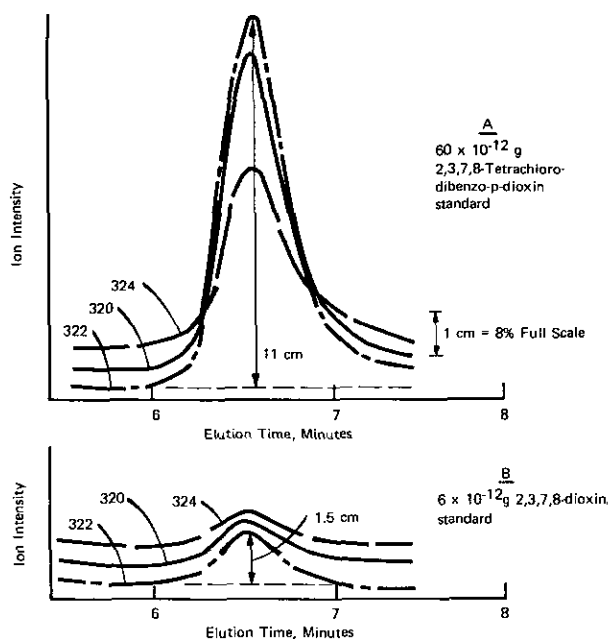
FIGURE 3. Gas chromatography–mass spectrometry for the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin at maximum sensitivity. Conditions: LKB 9000 GC-MS; column, 3% OV-210 on Chromosorb W-H.P.; resolution, ca. 400; sample, 6 μl of standard solutions.

The applicability of GC–MS for the determination of higher chlorinated dibenzo-p-dioxins has also been investigated. Table 7 illustrates the results of determination of hexachlorodibenzo-p-dioxin (two isomers) and octachlorodibenzo-p-dioxin by this procedure. Losses of either of these species have not been observed, as is apparent from the excellent recoveries obtained, either with the anion exchange or mixed-bed ion exchange procedures for matrix removal. As has been mentioned by several workers (17, 18), the presence of chlorinated phenoxyphenols can constitute a severe interference in some samples. Although these are not completely removed by a simple extraction from alkaline solution (14) (R. Bredeweg and W. Blaser, Dow Chemical Company, personal communication, 1973), the use of nonaqueous ion exchange does allow their complete removal. When the equivalent of 200 ppm of a mixture of heptachloro-, octachloro-, and nonachlorophenoxyphenols was subjected to either of the ion exchange cleanups, no interference was observed in the determination of hexachloro- or octachlorodibenzo-p-dioxin. If not removed, these materials represent

Table 3. Analytical scheme for determination of chlorinated dibenzo-p-dioxins.

	Sample		
	2,4,5-TCP 2,4,5-T Acid Pentachlorophenol	2,4,5-T Esters Fats Oils	Salts
Component determined	2,3,7,8-Dioxin Hexadioxin Octadioxin	2,3,7,8-Dioxin	Hexadioxin Octadioxin
Cleanup method	Dowex 21K–OH⁻ 1:1 benzene–methanol	Silica gel, 20% benzene in hexane	Dowex MR–3, 1:1 benzene–methanol
GC–MS detection method, amu	320:322:324 388:390:392 456:458:460	320:322:324	388:390:392 456:458:460
Detection limits, ppm	2,3,7,8–Dioxin Hexadioxin Octadioxin	0.05 0.1 0.5	
Time required per sample, hr	2,3,7,8–Dioxin Hexadioxin Octadioxin	2 4 4	

Table 4. Determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin: comparison of GLC methods with GC–MS.

Sample	2,3,7,8-tetra-chlorodibenzo-*p*-dioxin added, ppm	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin found, ppm	
		By GLC	By GC–MS
2,4,5-T Acid	0.00	<0.01	<0.01
	0.043	0.05	0.03
	0.086	0.09	0.09
	0.43	0.42	0.46
2,4,5-T Acid	0.00	0.13	0.11
2,4,5-TCP	0.00	0.03	0.03
	0.10	—	0.13
	0.10	—	0.13

a potential source of error for two reasons: they can dehydrohalogenate in the injection port of the GLC column to form a dibenzo-*p*-dioxin with one less chlorine, and they can produce a mass spectrum where M–HCl is a significant ion produced, which also constitutes an interference when monitoring the dibenzo-*p*-dioxin molecular ions.

Table 5. Determination of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin by gas chromatography-mass spectrometry.

Sample	2, 3, 7, 8-Dioxin	
	Added, ppm	Found, ppm
2,4,5-TCP A	0.00	<0.02
	0.06	0.05
	0.06	0.07
	0.06	0.06
	0.10	0.11
	0.10	0.11
2,4,5-TCP B	0.00	0.03
	0.10	0.13
	0.10	0.13
2,4,5-T Acid A	0.00	0.04
	0.24	0.30
2,4,5-T Acid B	0.00	0.41
	0.24	0.66
2,4,5-T Ester A	0.05	0.05
2,4,5-T Ester B	0.28	0.27
Orange Herbicide	0.05	0.06
Silvex Ester A	0.05	0.04
Silvex Ester B	0.28	0.24

The determination of chlorinated dibenzofurans by GC–MS can also be achieved by monitoring for the molecular ions of these species. However, when this was applied to the examination of some commercial pentachlorophenols, an interference was observed in the form of the chlorinated diphenyl oxides with two more chlorines than the furan of interest. These chlorinated diphenyl oxides elute from the GLC column at about the same time as the dibenzofuran with two less chlorine atoms. A major ion in the mass spectrum of the chlorinated diphenyl oxides, in addition to the molecular ion, is an ion corresponding to M–2CL. This fragment ion has the same exact mass and number of chlorines as the chlorinated dibenzofuran. These interferences are illustrated in Table 8.

This difficulty can be overcome by monitoring at mass 372 and 442 and subtracting from the mass 372 ion current an amount proportional to the chlorinated diphenyl oxide content calculated from mass 442. This requires separate injections for each chlorinated dibenzo-*p*-dioxin, since only three ions can be monitored at one time. Alternately, a GC–MS data acquisition system can be used to repetitively scan the whole mass spectrum (or a wide region of interest) and store the ion intensities for each mass for later examination (mass chromatography) (*19*).

Liquid column chromatography has been examined as a means of rapidly examining

Table 6. Determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in fat heated with chlorinated phenolic compounds.

| Compound added | Concentration in fat, ppm | Heating conditions | | Concentration of 2,3,7,8-dioxin, ppm |
		Temperature, °C	Time, hr	
2,4,5-TCP	1000	190	7	<0.05
	1000	190	14	<0.05
Sodium 2,4,5-TCP	1000	50	15	<0.05
	1000	190	7	<0.05
	1000	190	14	<0.05
Sodium 2,4,5-T Acid	1000	190	7	<0.05

Table 7. Determination of higher chlorinated dibenzo-p-dioxins by gas chromatography-mass spectrometry.

| Sample | Hexachlorodibenzo-p-dioxin | | Octachlorodibenzo-p-dioxin | |
	Added, ppm	Found, ppm	Added, ppm	Found, ppm
Solvents only	1.3	1.5	17	19
Pentachlorophenol	0.0	<0.5	0.0	14
	2.5	2.5	70	89
	13	14	350	360
	50	51	700	690
Sodium pentachlorophenate	0.0	<0.5	0.0	<5
	2.5	3.0	70	77
	13	13	350	350
	50	48	700	660
Mixed chlorophenoxyphenols (7, 8, and 9 chlorines)	0.0	<0.5	0.0	<5

Table 8. Potential interference of chlorinated diphenyl oxides in the determination of chlorinated dibenzofurans by GC-MS.

| Compound | Mass/charge | | Number of Cl | |
	M⁺	M-2Cl⁺	M⁺	M-2Cl⁺
Hexachlorodibenzofuran	372	—	6	—
Octachloro dibenzo-p-dioxin	442	372	8	6
Heptachlorodibenzofuran	406	—	7	—
Nonachloro dibenzo-p-dioxin	476	406	9	7
Octachlorodibenzofuran	440	—	8	—
Decachloro dibenzo-p-dioxin	510	440	10	8

pentachlorophenol produced to have a low content of chlorinated dibenzo-p-dioxins. The results of the use of "reversed-phase" liquid–liquid column chromatography (LCC) are shown in Figure 4. The lower trace is a standard mixture containing hexachlorodibenzo-p-dioxin at the equivalent of 2 ppm and octachlorodibenzo-p-dioxin at the equivalent of 12 ppm in the sample. The upper trace is the result of the injection of the neutral components of Dow improved penta-

chlorophenol (C. Pfieffer, Dow Chemical Company, personal communication, 1973). As can be seen, the hexachlorodibenzo-p-dioxin content is less than 0.5 ppm and the octachlorodibenzo-p-dioxin is 16 ppm. The concentration of heptachlorodibenzo-p-dioxin has not been calculated due to a lack of standards. The accuracy of liquid column chromatography for the determination of hexa- and octachlorodibenzo-p-dioxin is shown in Table 9. Excellent recoveries of
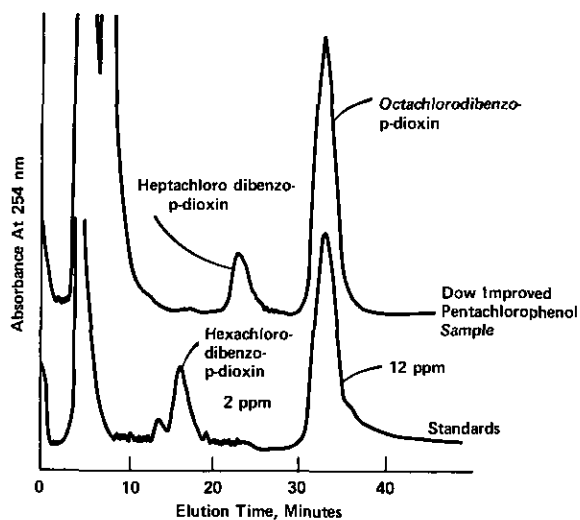
FIGURE 4. High speed liquid–liquid column chromatography of higher chlorinated dibenzo-*p*-dioxins. Conditions: column, ODS/Permaphase; 1000×2 mm; flow rate, 0.3 ml/min; sensitivity, 0.01/0.04 absolute units full scale; solvent, 14% H_2O in CH_3OH; sample, 2 μl of 10X concentrate.

both compounds were observed over the range of concentrations shown. It should be noted that attempts to use LCC for the examination of some commercial pentachlorophenol products produced chromatograms with interfering peaks in the region of hexachlorodibenzo-*p*-dioxin elution when the absorbance at 254 nm was monitored. GC–MS, with ion exchange "cleanup, was applicable to these types of samples, however.

Impact on Product Quality

The chronology of analytical methods at The Dow Chemical Company is shown in Table 10. As can be seen, increased analytical sensitivity and specificity for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin determination has been concurrent with decreased 2,3,7,8-dioxin content in manufactured material. The use of properly chosen and designed analytical measurement systems has permit-

Table 9. Determination of higher chlorinated dibenzo-*p*-dioxins by liquid column chromatography.

Sample	Hexachlorodibenzo-*p*-dioxin		Octachlorodibenzo-*p*-dioxin	
	Added, ppm	Found, ppm	Added, ppm	Found, ppm
Improved pentachlorophenol	0.00	<0.5		
	0.74	0.72		
	2.2	2.3		
	3.7	3.6		
	7.4	7.3		
Improved pentachlorophenol			0.0	16
			8.5	24
			17	33
			25	41

Table 10. Dow product improvement concurrent with analytical methods improvement.

Product	Analytical method		2,3,7,8-Dioxin concentration, ppm		
	Type	Date developed	Limit of detection	Production specification	Date of specification
2,4,5-Trichlorophenol	GLC	1964	1.0	<1.0	1966
	GLC	1970	0.5	<0.5	1970
	GC-MS	1971	0.05	<0.1	1971
2,4,5-T acid	GLC	1970	1.0	<1.0	1970
	GC-MS	1971	0.05	<0.1	1972
2,4,5-T esters	GC	1970	1.0	<1.0	1970
	GC-MS	1971	0.05	<0.1	1972

ted an accurate assessment of the quality of manufactured material. This has resulted in a tenfold decrease in the maximum allowable concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin in these products. Similar improvements in analytical methods will allow equivalent or greater improvements in the quality of higher chlorinated phenols.

Summary

The use of simple cleanup methods in the examination of samples suspected to contain chlorinated dibenzo-p-dioxin and dibenzofurans coupled with selective detection via GC–MS results in determinations which are both accurate and sensitive. Under these conditions, recovery of standards is high to part per billion concentration levels, and the certainly associated with the results is correspondingly high. Although other methods can be applied to selected samples, results on samples of unknown origin should be examined by GC–MS to avoid interferences.

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