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DETERMINATION OF CHLORINATED DIBENZO-*p*-DIOXIN CONTAMINANTS IN 2,4-D PRODUCTS BY GAS CHROMATOGRAPHY–MASS SPECTROMETRIC TECHNIQUES

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SUMMARY

An analytical procedure is presented which permits the routine determination of mono- to tetrachlorodibenzo-*p*-dioxins down to the 1 ppb* level in technical and formulated products of 2,4-D acids, esters and amine salts. Methods involved extraction, partitioning, silica gel and basic alumina multiple column clean-up with final quantitation being performed by gas chromatography–mass spectrometry using a 3% SE-30 packed column. Isomer identification was achieved on SP2100 and SE-54 capillary columns while dioxin identity was confirmed using accurate mass measurements from full scan mass spectrometry at 10,000–20,000 resolution. A survey of 58 2,4-D samples representing 1980 Canadian supplies showed the presence of 2,7-dichloro-, 1,3,7-trichloro- and 1,3,6,8-/1,3,7,9-tetrachlorodioxions in 2,4-D esters and amine products. Of 26 2,4-D amines tested the majority (18 samples or 70%) contained no dioxin contamination above the 1 ppb level while all but 1 of the 21 2,4-D esters analyzed contained levels of dioxin ranging from 5 ppb to 23.8 ppm. None of the 11 2,4-D technical acids investigated contained any dioxin contamination, however, low levels of mono- to tetrachlorobiphenyl ethers were observed.

INTRODUCTION

The class of compounds known collectively as the polychlorinated dibenzo-*p*-dioxins (PCDDs) have become a major concern since the late 1960s/early 1970s when 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), with its extremely toxic and teratogenic properties, was found to occur as a microcontaminant in the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)[1–3]. Levels in the technical material ranged from 0.1 to 55 ppm 2,3,7,8-TCDD[1]. Also, the identification and quantitation of 2,3,7,8-TCDD and other dioxin isomers have been reported in 2,4,5-T formulations originating from Europe in the 1960s and from Herbicide Orange mixtures (*i.e.* 1:1 mixture of the butyl esters of 2,4-D and 2,4,5-T)[4]. In a recent British study of 30

* Throughout this article the American billion (10^9) and trillion (10^{12}) are meant.

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2,4,5-T samples (acids, esters and formulated products), 12 contained levels of 2,3,7,8-TCDD in the range 0.01–0.08 mg/kg (*i.e.* 10–80 ppb)[5].

In parallel with the analytical investigations into the dioxin content of 2,4,5-T, other industrial and agricultural chemicals based on chlorophenols have been studied, such as, pentachlorophenol, hexachlorophene and other chlorinated phenoxy acid herbicides, and recent reviews have summarized the current situation[6,7]. In the area of the lower chlorinated phenols and phenoxyacetic acids no PCDDs were found in 2,4- and 2,6-dichlorophenol[8], while Woolson *et al.*[9] reported a hexachlorodioxin (HxCDD) in 1 sample of 2,4-D at a level between 0.5–10 ppm. Only tetra, hexa-, hepta- and octachlorodioxin results were reported and none observed (above the 0.5-ppm limit of detection) in 23 other 2,4-D samples, as well as three 2,4-DB and two 2,4-DEP. Similarly no di- to hexa-CDD isomers were found in older Scandinavian formulation of 2,4-D although one sample did contain 0.06 ppm of a tetrachlorodibenzofuran (TCDF)[10].

The herbicide 2,4-D is widely used in Canada and it is effective in controlling broad-leaf weeds in lawns, cereal fields, etc. As part of a re-evaluation program concerning microcontaminants in pesticide formulations initial results on 2,4-D revealed the presence of di, tri- and tetra-CDDs in some products on the Canadian market[11]. In this paper a more comprehensive study of this on-going program is presented.

EXPERIMENTAL

Reagents

Silica gel (M. Kieselgel 60; Merck, Darmstadt, G.F.R.) activated overnight at 125°C. Basic alumina (Activity I; Woelm, Eschwege,G.F.R.) as received. Hexane, dichloromethane, methanol and acetronitrile were pesticide grade, glass distilled (Caledon Laboratories, Georgetown, Canada). All glassware was detergent washed, rinsed with water, acetone, de-ionized water and heated at 275°C in a forced air oven for 8–16 h before use.

Gas chromatography–mass spectrometric analysis

Initial screening and subsequent quantitation was performed on 3 ft. × $\frac{1}{4}$ in. 3%SE-30 ultra-phase on Chrom 750 coupled to a Finnigan 4000 quadrupole mass spectrometer equipped with an INCOS data system. The packed gas chromatographic (GC) column was temperature programmed from 205–225°C at 5°C/min using a carrier flow of 20 ml/min. Also a 25 m × 0.2 mm fused silica capillary column coated with SP2100 (Hewlett Packard, Avondale, CA, U.S.A.) and a 30 m × 0.2 mm capillary column coated with SE-54 (Chromatographic Specialties, Brockville, Canada) were utilized using temperature programming as follows: 60°C, 1 min isothermal then 8°C/min to 220°C. Samples (1–5 μl) were splitlessly injected at a 20 p.s.i. column head pressure. PCDDs were monitored using specific masses —*m/e* 218 and 220 for isomers of monochloro-, 252 and 254 for dichloro-; 286 and 288 for trichloro- and 320 and 322 for tetrachlorodioxins. Specific isomers were identified by comparing their column retention with reference compounds and confirmed by high-resolution mass spectrometry (MS) analysis via elemental composition and fragmentation patterns. The lower limit of detection was 1 ppb.

For high-resolution GC–MS analysis, the gas chromatograph was equipped

with a 6 ft. × 1/4 in. glass column packed with either 3% SE-30 ultra-phase on Chrom 750 (80–100 mesh) or 3% OV-17 on Chrom 750 which was coupled to a Kratos MS-50 mass spectrometer by means of a single stage glass jet separator. The GC columns were temperature programmed from 200 to 275°C at 4°C/min. Single ion monitoring was carried out at *m/e* 321.8936 at a resolution of 20,000 (10% valley) for tetrachlorodioxins. Source temperature 250°C, separator 300°C, emission current 500 μA, accelerating voltage 8.0 kV, detection limit $20 \cdot 10^{-12}$ g. Full scan data was acquired at 10,000 resolution using the INCOS data system. The major peaks of the isotopic chlorine cluster were all within ± 10 ppm of the correct mass value.

Sample preparation

2,4-D Esters. A 2-g sample was transferred onto a silica gel column (50 g in a 60 × 2.0 cm I.D. glass column). The column was eluted with 150 ml of 30% dichloromethane–hexane and the first 30 ml were discarded. The remaining eluate was collected in a 250-ml round-bottomed flask and concentrated to 1–2 ml on a rotary evaporator prior to alumina column clean-up.

2,4-D Acids. A 10-g sample was dissolved in 400 ml of a acetonitrile–water (1:1) mixture in a 500-ml flask, to which had been added 40 ml methanol. The solution was transferred to a 1000-ml separatory funnel using 2 rinsings of 50 ml hexane to wash the flask. After partitioning three times with 100-ml portions of hexane the layers were combined. The organic layer was washed twice with 50 ml methanol–water (1:1) and the rinsings were discarded. The hexane layer was dried by passing it through 30 g of pre-washed sodium sulfate in a funnel; then it was concentrated to 1–2 ml under reduced pressure and proceeded to the alumina column clean-up.

2,4-D Amines. A 2.0–2.5-g amount of sample was transferred into a 250-ml flask and 100 ml water were added together with a clean magnetic stirring bar and the solution was allowed to mix thoroughly for 10 min. The flask contents were transferred to a 250-ml separatory funnel and partioned three times with 25 ml hexane. The organic layers were combined, washed twice with 20-ml water, dried by passage through 15 g pre-washed sodium sulfate and concentrated to 1–2 ml prior to alumina column clean-up.

Alumina column clean-up. A basic alumina column (15 g in a 25 × 1.5 cm I.D. glass column) was prepared by adding the alumina to a 0.5 cm column of Ottawa standard sand packed above a small glass wool plug. The alumina was washed down and topped with a 0.5-cm height of sodium sulfate. The concentrates obtained were transferred quantitatively above on to the alumina column with 3 × 2 ml hexane washings. The column was eluted with (1) 100 ml hexane. (2) 100 ml dichloromethane–hexane (2:98), (3) 100 ml dichloromethane–hexane (5:95) and (4) 100 ml dichloromethane–hexane (10:90). Fractions (1) and (2) were discarded while (3) and (4) were collected and concentrated to 1–2 ml and transferred to a 5-ml graduated centrifuge tube with 3 × 1 ml washings of benzene. The concentrate was evaporated to dryness with nitrogen and dissolved in 0.1–0.5 ml volumes of hexane.

High-performance liquid chromatography (HPLC) analysis

A Waters Assoc. Model 6000A solvent delivery system was equipped with a Waters Assoc. U6K universal injector and an electrochemical detector (LCEC; Bioanalytical Systems, West Lafayette, IN, U.S.A.) employing a glassy carbon electrode (TL-5) and reference electrode (R.E. I) set at a positive voltage of 0.85 V, sensitivity

0.5 nA/V, and a background current offset of 10^3 nA. A 25 cm × 4.6 mm I.D. column packed with μLiChrosorb RP-18 10-μm material (Brownlee Labs., Santa Clara, CA, U.S.A.) was connected to a 7.6 cm × 2 mm Co:Pell ODS guard column (Whatman, Clifton, NJ, U.S.A.). The mobile phase was an acetonitrile–0.03 *M* buffer solution (0.03 *M* NaH_2PO_4 in deionised water) (35:65) adjusted to pH 5.45 and flowing at 2.7 ml/min.

Recovery

Recovery experiments were carried out by adding differing amounts of 1-monochlorodioxin, 2,7-dichlorodioxin, 1,3,6,8-, 2,3,7,8- and 1,2,3,4-TCDD to 2,4-D acid and ester technical products and to 2,4-D ester and amine formulations. Fortifications levels ranged from 1–1000 ppb for 2,7-DCDD and 1,2,3,4-TCDD while a narrower range (1–250 ppb) was covered using the 1-mono-, 1,3,6,8-tetra- and 2,3,7,8-tetra-CDDs. Recoveries ranged from 85–106% for the di- and tetra-CDDs while for the 1-MCDD recoveries of 71–99% were obtained at levels corresponding to 1–100 ppb. Throughout the course of sample analysis spiking with 1,2,3,4-TCDD in the range 1–100 ppb, was carried out daily and the average recovery over a 4-month period was 90.5%.

RESULTS AND DISCUSSION

The double column clean-up method described above gave sufficiently clean GC–MS chromatograms (Fig. 1) to allow a routine quantitative detection limit of 1

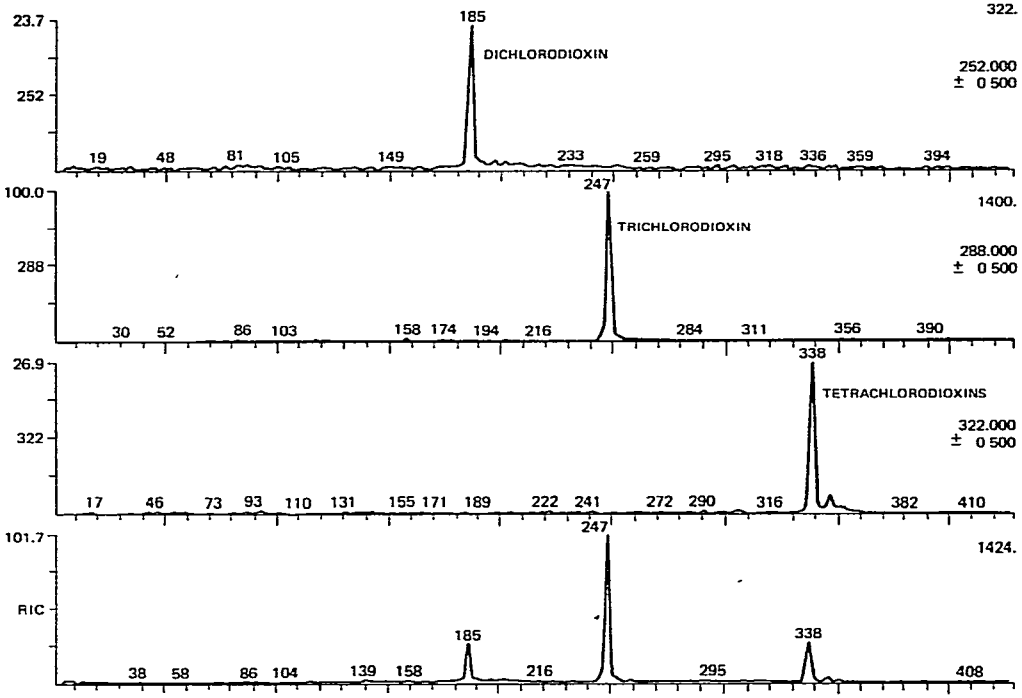

Fig. 1. GC–MS monitoring of a typical 2,4-D isooctyl ester formulation showing the elution of di, tri- and tetra-CDDs on a 25 m SP2100 capillary column. Single-ion monitoring was via low-resolution quadrupole MS.

ppb with recoveries in excess of 85% for the di- to tetra-CDDs studied. By adjusting the volume of the final extracts to 100 μl a lower screening limit of 500 ppt for the 2-g ester and amine samples and 100 ppt for the 10-g acid samples was achievable. The elution pattern given for the 2,4-D samples on alumina was also found adequate in all instances except one. One batch of dichloromethane solvent necessitated a change in the established regime due to only partial elution of 2,7-DCDD in the 100-ml dichloromethane–hexane (10:90) fraction resulting in a 26% recovery. A modification in elution pattern to 100 ml hexane plus 100 ml dichloromethane–hexane (2:98) which were discarded, followed by 150 ml dichloromethane–hexane (10:90) plus 50 ml dichloromethane–hexane (30:70) allowed collection of all dioxins including octachlorodioxin. The problem with the dichloromethane was tentatively traced to a hypochlorite contaminant which altered the absorption characteristics of the basic alumina used.

Initially, eleven 2,4-D technical acids from various sources were analyzed for mono- to tetra-CDDs down to the 1-ppb level and none were observed. However, distinct patterns of contaminants were observed in all samples and the major components were shown to be a series of isomeric chlorobiphenyl ethers, containing from 1 to 4 chlorine atoms, by comparison with authentic standards. Since Woolson *et al.*[9] had previously reported the presence of a HxCDD in a 2,4-D sample, the 11 technical acids were reanalyzed, using the revised elution scheme described above for the isolation of mono- to octachlorodioxin, and none was found above a detection limit of 10

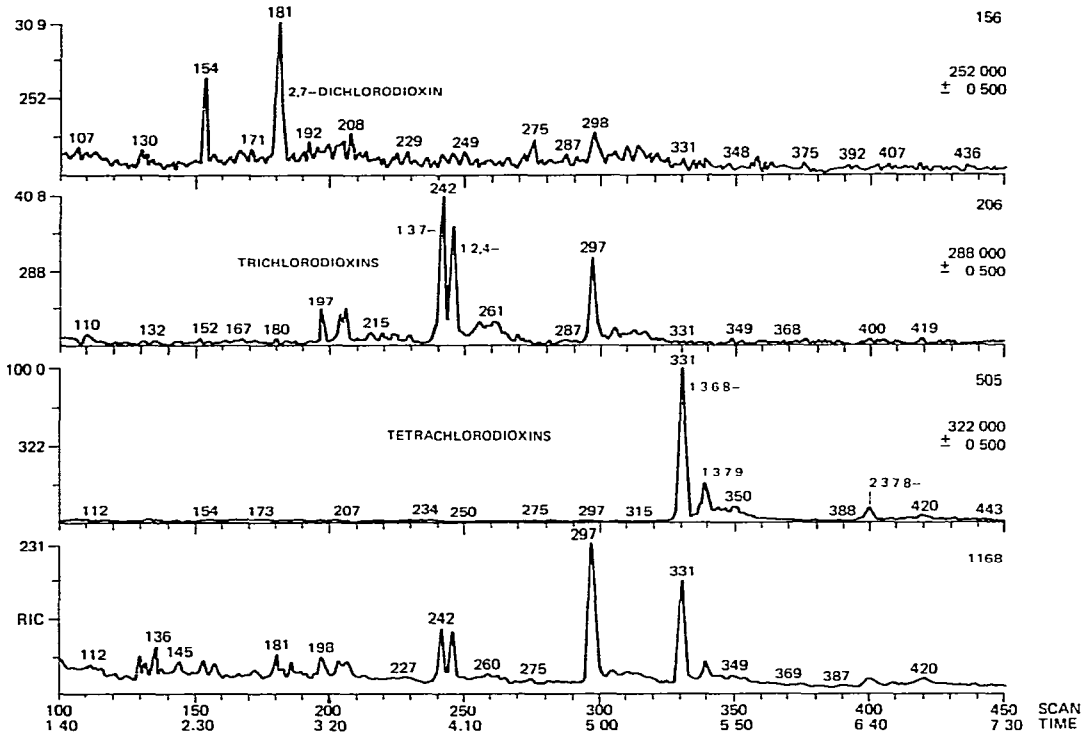

Fig. 2. GC–MS chromatogram of a mixed butyl ester formulation of 2,4-D fortified with 2,7-DCDD (50 ppb), 1,2,4-Tri-CDD (25 ppb) and 2,3,7,8-TCDD (10 ppb). Column: 25 m SP2100 at 225°C.

ppb. The GC–MS monitoring of 2,4-D isooctyl ester samples, however, showed the presence of a di-, tri- and two tetra-CDDs (Fig. 1). Using standard spiking techniques 2,7-DCDD, 1,2,4-tri-CDD and 2,3,7,8-TCDD were added to a typical 2,4-D mixed butyl ester sample and it was established that the tri-CDD present in the sample appeared 10 sec ahead of the 1,2,4-tri-CDD standard (Fig. 2). The use of 2,7-DCDD increased the peak height of the DCDD already present while the two TCDDs present in the sample had retention times of 0.81 and 0.84 relative to 2,3,7,8-TCDD on the capillary SP2100 column. From the relative retention characteristics on a 3% SE-30 packed column, the SP2100 and SE-54 (*i.e.* 0.90 and 0.915, respectively) capillary columns, these two TCDDs were tentatively identified as the 1,3,6,8- and 1,3,7,9-isomers[12,13]. This was confirmed by synthesis and comparison with authentic standards prepared from the condensation of 2,4,6-trichlorophenol under alkaline reflux conditions[14]. The 1,3,6,8-/1,3,7,9-TCDD isomers were well resolved from the 1,2,3,4- and 2,3,7,8-isomers on both packed and capillary columns (Fig. 3). On the 3% SE-30 packed column the 1,3,6,8-/1,3,7,9-isomers appeared as one peak and this was the method of choice for subsequent quantitative analysis. Support for the identification of 1,3,6,8-TCDD in the 2,4-D ester and amine samples was obtained through accurate mass measurement of the molecular ion cluster of *m/z* 320 through 326 as observed from peak 338 (Fig. 1). The experimentally determined masses of seven ions of this cluster, including those due to the ^{13}C isotope contributions, were all within 1 millimass unit (mmu) or 3 ppm, as shown in Fig. 4, for the molecular formula $C_{12}H_4O_2Cl_4$. In addition, the loss of COCl from the molecular ion is confirmed by the accurate masses at *m/z* 257 to 261 which indicate the fragment formula $C_{11}H_4OCl_3$ to within 1.7 mmu. Similarly, the fragmentation pattern obtained from sample and synthesised standard were identical over the mass range *m/z* 50–326.

The manufacture of 2,4-D acid involves the reaction of 2,4-dichlorophenol with chloroacetic acid under basic aqueous conditions[15]. Since the formation of 1,3,6,8-

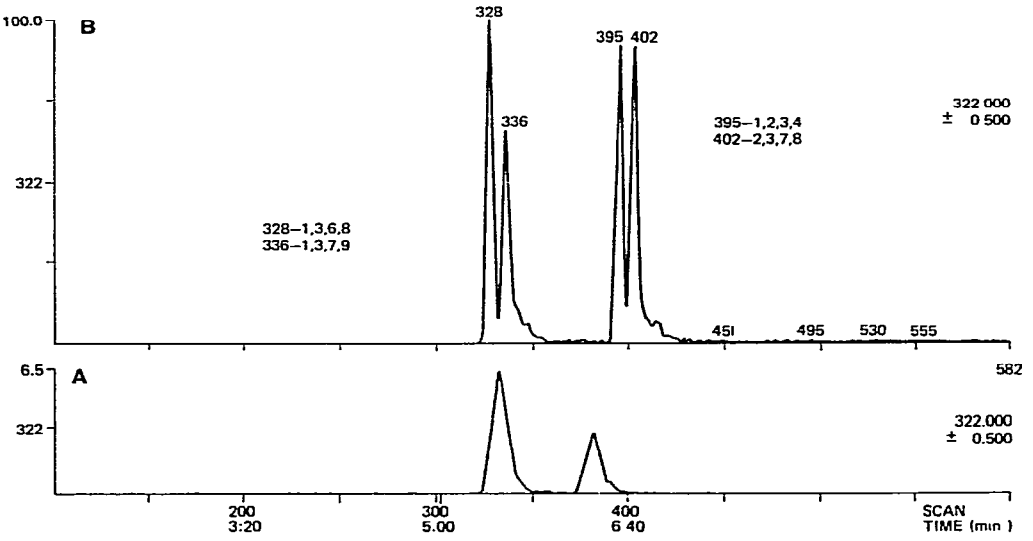

Fig. 3. Chromatograms showing the separation of four tetrachlorodioxin isomers on A, 1 m × 2 mm 3% SE-30 ultra phase packed column and B, 25 m SP2100 fused silica capillary column.

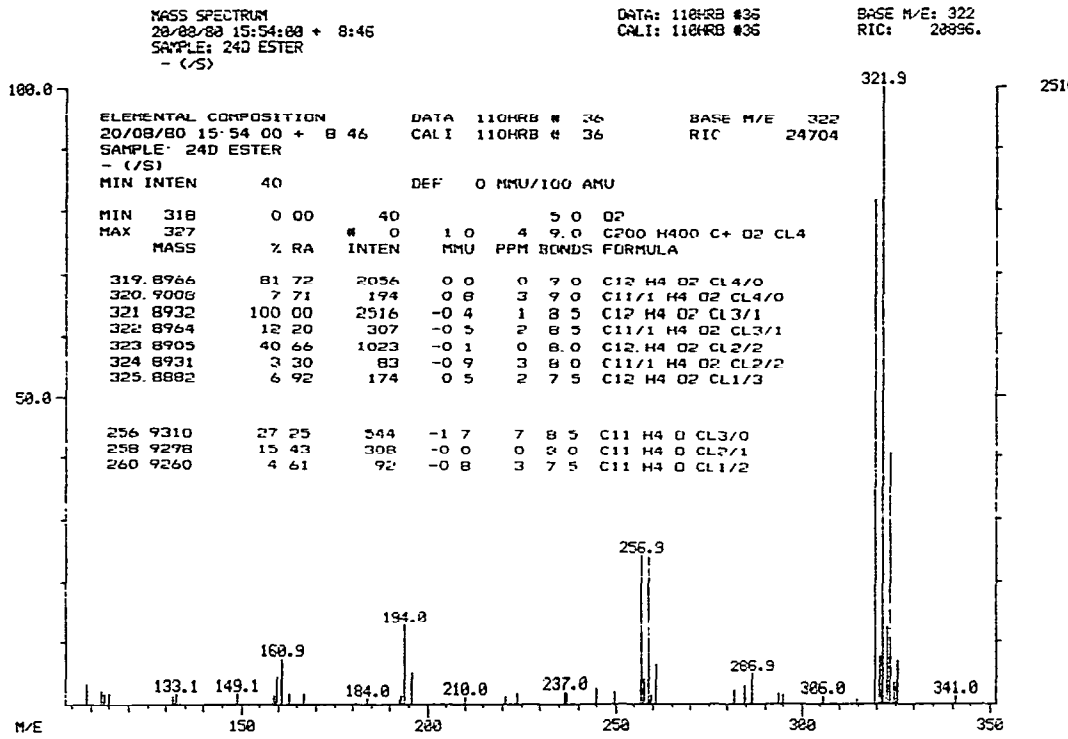

Fig. 4. Kratos MS-50 high-resolution mass spectrum of 1,3,6,8-tetrachlorodioxin from a 2,4-D isooctylester sample together with accurate mass measurements on m/z 320, 322 and 324 ions.

TCDD and its Smiles rearranged isomer, 1,3,7,9-TCDD, necessitates the presence of 2,4,6-trichlorophenol, the purity of technical 2,4-dichlorophenol (2,4-DCP) was investigated. HPLC analysis was carried out using a μLiChrosorb RP-18 reversed-phase column with electrochemical detection and showed that in addition to 2,4-DCP (86.22%) the technical material contained appreciable levels of the *o*- and *p*-monochlorophenols, 1,85%, the products of under chlorination, as well as, 3.23% of 2,4,6-TCP, the over chlorination product (Fig. 5). Interestingly, this particular technical 2,4-DCP sample has a 5.64% level of the isomeric 2,6-DCP also present. Leng[16] postulated that the occurance of the expected 2,7-DCDD isomer in 2,4-DCP would be unlikely since 2,4-DCP is produced under acidic conditions. The technical 2,4-DCP investigated in this study was analyzed for dioxin content and none were found. However, in an effort to identify the tri-CDD observed in the 2,4-D ester and amine samples, 2,4-DCP and 2,4,6-TCP were condensed under alkaline reflux condition and a dioxin pattern identical to that observed on the 2,4-D samples (Fig. 1) was obtained. Therefore, the tri-CDD is either the 1,3,7- or 1,3,8-isomer as expected from the above condensation reaction. On all packed and capillary columns investigated, only a single tri-CDD peak was observed for both synthetic standard and 2,4-D samples. Similarly, a comparison of the high resolution mass spectra of the synthesized tri-CDD and that found in the samples were identical. The mass spectral difference between the 3:0 (*i.e.* 1,2,4-isomer) and the 2:1 (*i.e.* 1,3,7-isomer) ring, chlorine substi-

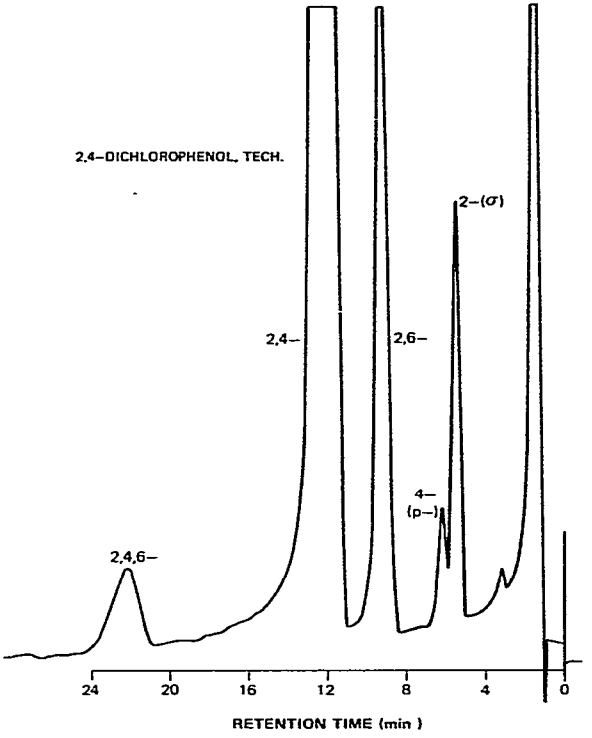

Fig. 5. Separation of technical 2,4-dichlorophenol by reversed-phase HPLC. Column: μLiChrosorb RP-18. Mobile phase: 35% acetonitrile–0.03 *M* buffer solution flowing at 2.7 ml/min.

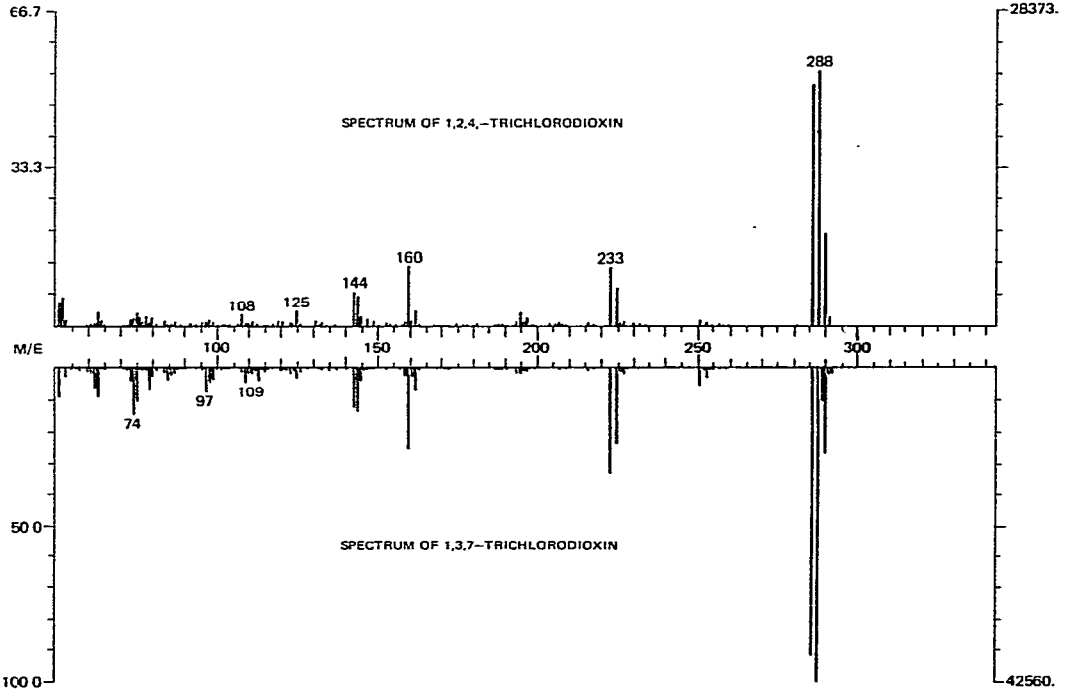

Fig. 6. Comparison of the low-resolution mass-spectra of two trichlorodioxins with 3:0 (1,2,4-) and 2:1 (1,3,7-) ring chlorine substitution.

tution becomes very apparent in the *m/z* 50–150 range as shown in Fig. 6[17]. Very few distinctive fragment ions are observed below *m/z* 144 in the 1,2,4-TCDD spectrum while characteristic peaks at *m/z* 74, 97 and 109 are useful in identification of the 1,3,7-isomer.

The levels of PCDDs found in 26 2,4-D amine salt samples and 21 2,4-D ester samples are given in Tables I and II. These results represent dioxin contamination of 2,4-D technical and formulated products as was available in the Canadian marketplace in 1980. Since these formulations contained varying amounts of active ingredients the quantitation of the di-, tri- and tetra-CDDs was based on 2,4-D % (w/w) acid equivalent as obtained by isomer-specific HPLC analysis. Of the 26 2,4-D amine samples tested (Table I) the majority (*i.e.* 18 samples or 70%) contained no dioxin contamination above the detection limit of 1 ppb. The remaining 8 samples gave dioxin results ranging from 5–409 ppb 2,7-DCDD, 38–587 ppb 1,3,7-tri-CCD and 20–278 ppb for the combined 1,3,6,8- and 1,3,7,9-TCDD isomers. Conversely (Table II) in the case of the 2,4-D esters all but one of the 21 samples tested contained

TABLE I

LEVELS OF DI-, TRI- AND TETRACHLORODIOXINS IN 2,4-D AMINE FORMULATIONS

– Indicates none detected above 1 ppb.

Sample No.	*Ingredient label guarantee (oz. 2,4-D amine per gallon)*	*2,4-D acid % (w/w)*	*Dioxin* (ppb)*		
			2,7-di-	*1,3,7-tri-*	*1,3,6,8-/1,3,7,9-tetra-*
1	80	44.6	–	–	–
2	80	–	–	–	–
3	80	–	–	–	–
4	80	41.3	–	–	–
5	80	–	–	–	–
6	80	41.7	–	–	–
7	80	37.9	–	–	–
8	80	–	–	–	–
9	80	42.44	316	490	132
10	80	43.10	275	587	136
11	80	–	–	–	–
12	80	–	–	–	–
13	80	42.9	409	551	210
14	80	42.9	–	–	–
15	80	–	–	–	–
16	80	–	–	–	–
17	80	–	–	–	–
18	80	–	–	–	
19	80	42.55	140	230	96
20	80	42.66	–	38	54
21	80	42.74	–	584	278
22	80	42.74	5	54	20
23	96	49.59	33	533	208
24	80	42.74	–	–	–
25	80	–	–	–	–
26	80	–	–	–	–

* All dioxin results are based on 2,4-D acid % (w/w).

appreciable levels of dioxin contamination. This study covered the isooctyl ester (IOE), mixed butyl ester (MBE) and propylene glycol butyl ester (PGBE) types. Dioxin levels ranged from 104 ppb–23.8 ppm 2,7-DCDD, 35 ppb–2.45 ppm 1,3,7-tri-CDD and 120 ppb–8.7 ppm TCDD. No other dioxin isomers, other than those mentioned above, were found in these samples.

TABLE II

LEVEL OF DI- TRI- AND TETRACHLORODIOXINS IN 2,4-D ESTERS PRODUCTS

– Indicates none detected above 1 ppb.

Sample No.	*Ingredient*	*Label guarantee (oz./gal.)*	*2,4-D acid % (w/w)*	*Dioxin* (ppb)*		
				2,7-di-	*1,3,7-tri-*	*1,3,6,8-/1,3,7,9-tetra-*
1	2,4-D IOE	80	48.1	**	**	384
2	2,4-D IOE	80	42.9	8474	2450	8730
3	2,4-D IOE	96	55.2	674	422	466
4	2,4-D IOE	96	55.0	110	385	127
5	2,4-D IOE	96	55.0	362	1053	414
6	2,4-D IOE	96	52.36	**	346	226
7	2,4-D IOE	96	52.17	2722	2079	717
8	2,4-D IOE	80	46.55	4200	1632	1752
9	2,4-D IOE	65.1%	–	104	639	315
10	2,4-D IOE	80	45.46	1238	1825	852
11	2,4-D IOE	112	61.57	109	929	486
12	2,4-D IOE	96	54.30	151	102	120
13	2,4-D MBE	128	68.3	23815	273	219
14	2,4-D MBE	128	67.2	503	659	311
15	2,4-D MBE	128	69.5	7295	371	314
16	2,4-D MBE	128	67.8	293	385	175
17	2,4-D MBE	TECH	–	**	**	317
18	2,4-D MBE	80	47.26	–	–	–
19	2,4-D MBE	128	67.68	151	102	120
20	2,4-D MBE	128	67.57	264	35	148
21	2,4-D PGBE	80	48.8	134	418	384

* All dioxin results are based on 2,4-D acid % (w/w).
** Levels not given due to interferences.

The dioxin results reported in this study differ from those found in earlier 2,4-D investigations[9,10]. Present results showed that 11 2,4-D technical acids were consistently dioxin free and in addition there was a clear distinction between the dioxin contents of the ester and amine product types investigated. While significant variations exist between individual samples taken at different times, the present analyses tend to indicate different manufacturing procedures for basic or technical materials. The classic manufacturing method for 2,4-D involves production of the acid which is then converted to the usable amine or ester product[15]. However, there are other manufacturing procedures[18] and it may be these other processes which are responsible for the dioxin contamination.

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REFERENCES

1 R. W. Storherr, R. R. Watts, A. M. Gardner and T. Osgood, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 218.
2 C. S. Helling, A. R. Isensee, E. A. Woolson, P. D. Ensor, G. E. Jones, J. R. Plommer and P. C. Kearney, *J. Environ. Qual.*, 2 (1973) 171.
3 D. A. Elvidge, *Analyst (London)*, 96 (1971) 721–727.
4 C. Rappe, H. P. Buser and H. P. Bosshardt, *Chemosphere*, 5 (1978) 431–438.
5 Advisory Committee on Pesticides, *Further Review of the Safety for Use in the UK of the Herbicide 2,4,5-T*, Pesticides Branch, Ministry of Agriculture, Fisheries and Food, London, December 1980.
6 D. Firestone, *U.S. Food Drug Adm. By-Lines*, 2 (1977) 57–89.
7 C. Rappe, H. R. Buser and H. P. Bosshardt, *Proceedings of the CIPAC Symposium, Baltimore, U.S.A., June 5–7, 1979*, Heffers Printers, Cambridge, Great Britain.
8 D. Firestone, J. Ress, N. L. Brown, R. P. Barron and J. N. Damico, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 85–92.
9 E. A. Woolson, R. F. Thomas and P. D. J. Ensor, *J. Agr. Food Chem.*, 20 (1972) 351–354.
10 A. Norstrom, C. Rappe, R. Lindahl and H. R. Buser, *Scand. J. Work Environ. Health*, 5 (1979) 375–378.
11 W. P. Cochrane, J. Singh, W. Miles, B. Wakeford, J. Scott, *Proceedings of Impact of Chlorinated Dioxins and Related Compounds on the Environment Symposium, Rome, Italy, October 22–24, 1980*, Pergamon, Oxford.
12 C. Rappe, H. R. Buser, and H. P. Bosshardt, *Chemosphere*, 5 (1978) 431–438.
13 T. J. Nestrick..L. L. Lamparski and R. H. Stehl, *Anal. Chem.*, 51 (1979) 2273–2281.
14 A. S. Kende, J. J. Wade, D. Ridge and A. Poland, *J. Org. Chem.*, 39 (1974) 931–937.
15 P. C. Kearney and D. D. Kaufman, *Herbicides*, Vol. I, Marcel Dekker, New York, 1975, pp. 8–10.
16 M. L. Leng, *Proceedings of the CIPAC Symposium, Baltimore, Maryland, U.S.A., June 5–7, 1979*, Heffers Printers, Cambridge, Great Britain.
17 H. R. Buser and C. Rappe, *Chemosphere*, 2 (1978) 199–211.
18 National Research Council of Canada, Associate Committee on Scientific Criteria for Environmental Quality Publication, *Phenoxy Herbicides — Their Effects on Environmental Quality*, NRCC No. 16075, Ottawa, 1978, p. 218.