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# Multispectral Identification of Alkyl and Chloroalkyl Phosphates from an Industrial Effluent\*

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Multispectral techniques (gas chromatography combined with low and high resolution electron-impact mass spectrometry, low and high resolution chemical ionization mass spectrometry, and Fourier transform infrared spectroscopy) were used to identify 13 alkyl and chloroalkyl phosphates in a water sample taken from the effluent of a plant that manufactures fire-retardant chemicals. Of the 13 phosphates identified, only 4 were located in library mass spectral data bases; thus, techniques other than conventional low resolution electron-impact mass spectrometry with data base matching were required. Several of the identified phosphates are commonly used fire retardants; however, three exhibited chemical structures different from those of the commercially manufactured fire retardants and the reactants used in their synthesis. (*J Am Soc Mass Spectrom* 1991, 2, 419-426)

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Under the Clean Water Act Amendments of 1987, the U.S. Environmental Protection Agency continually reviews the occurrence of potentially harmful chemicals in industrial waste waters. Selected waste effluents are analyzed to identify chemicals that have not been identified previously either because they were not present or because improvements in identification methods permit their detection and identification for the first time. Recently, organic extracts of samples taken from several plants manufacturing organic chemicals were analyzed by using multispectral identification techniques not generally applied previously. Among the plants sampled was a plant that manufactures fire retardants.

Alkyl, haloalkyl, and aryl phosphates have been widely used as flame retardants in a variety of products. The more common aryl phosphates are found in plasticizers, lubricants, and hydraulic fluids [1, 2]. The chloroalkyl phosphates have been used in both fabrics and insulation materials [3, 4]. Although production of chloroalkyl phosphates is considerable (24 million pounds in 1985 [5]), relatively few identifications of these compounds in the environment have been made. Among the reports are citations of chloroalkyl

phosphates in the United States from the Mississippi River and New Orleans drinking water [6, 7]; in Japan from river water, sea water, and sediment [8]; and in Canada in drinking water [9]. Chloroalkyl phosphates have also been located in human seminal plasma [3]. Many studies have been performed to determine the toxicity of these phosphates [10], as warranted by their widespread use in fabrics, plasticizers, hydraulic fluids, and lubricants. The results showed phosphates to be absorbed into the body [2, 3, 11, 12] and to be toxic to fish [13, 14].

This article discusses the identification of 13 alkyl and chloroalkyl phosphates and demonstrates how multispectral analysis can be used to identify organic compounds in environmental samples. Multispectral techniques—gas chromatography combined with high and low resolution electron-impact mass spectrometry (GC/EI-MS), high and low resolution chemical ionization mass spectrometry (GC/CI-MS), and Fourier transform infrared (GC/FT-IR) spectroscopy—provided structural information that permitted the identification of these alkyl phosphates. These identifications could not have been made by using conventional low resolution EI-MS alone.

## Experimental

**Sample collection.** Sample extracts were obtained through the Industrial Technology Division of the U.S. Environmental Protection Agency's Office of

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**Water.** Samples were collected from the effluent of a plant that manufactures fire-retardant chemicals and were prepared according to EPA Method 1625C [15], which produced an acid and a base/neutral extract.

**Materials.** A standard of tris(1,3-dichloro-2-propyl)phosphate was purchased from Chem Service, Inc. (West Chester, PA). 1,2-Bis[bis(2-chloroethyl)-phosphato]ethane was obtained from Olin Chemicals (Stamford, CT).

**GC/MS analysis.** GC/MS analyses were performed on a VG 70-SEQ high resolution hybrid mass spectrometer (VG Instruments, Manchester, UK) equipped with the VAX-based OPUS data system and a Hewlett Packard Model 5890A gas chromatograph (Palo Alto, CA). The mass spectrometer was operated at an accelerating voltage of 8 kV and at resolutions of 1000 and 6000 for low and high resolution experiments, respectively. Positive CI experiments were done by using methane gas. Injections of 1 to 2.5  $\mu$ L of the extract were introduced onto a split/splitless injector and a J & W DB-5 chromatographic column (J & W Scientific, Folsom, CA) (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film). The injector temperature was 230  $^{\circ}$ C, and the transfer line was held at 260  $^{\circ}$ C. The GC program had an initial temperature of 40  $^{\circ}$ C held for 5 min and increased at a rate of 8  $^{\circ}$ C/min to 280  $^{\circ}$ C, and held for 20 min. Helium was used as the carrier gas at a linear velocity of 23 cm/sec.

**GC/FT-IR analysis.** The GC/FT-IR analyses were performed by using a Digilab Model FTS-60- FT-IR spectrometer equipped with a Digilab Model 3200 FT-IR workstation (Digilab Division of Biorad, Cambridge, MA) and a Hewlett Packard Model 5890 gas chromatograph with a cool on-column injector. The FT-IR spectrometer had a Model GC/C 32 light-pipe-based interface equipped with a narrow band mercury-cadmium-telluride detector. Spectra generated had 8  $\text{cm}^{-1}$  resolution with a useful range of 4000 to 700  $\text{cm}^{-1}$ . The GC column used was a J & W DB-5 Megabore column (30 m  $\times$  0.53 mm i.d., 1.5  $\mu$ m film); temperature program was 5 min at 40  $^{\circ}$ C, then at 8  $^{\circ}$ C/min to 280  $^{\circ}$ C, and held for 30 min; carrier gas was helium at a linear velocity of 22 cm/sec. The FT-IR interface was held at 280  $^{\circ}$ C for both the light pipe and transfer lines.

## Results

The conventional method for identifying organic compounds found in the environment—low resolution EI-MS with library data base matching—was only partially beneficial to the identification of the phosphates found in this industrial effluent. Only 4 of the 13 phosphates gave good library data base matches, which do not necessarily guarantee valid identifications. Therefore, techniques other than low resolution

EI-MS were necessary to elucidate most of these phosphate structures. As a result of examining fragmentation patterns and isotopic ratios evident in the low resolution EI spectra, some tentative structural assignments were initially proposed. Pure standards were available for only two of these.

The low resolution GC/MS total ion current chromatogram obtained for the base/neutral extract under EI conditions is shown in Figure 1a. Peaks labeled 1 through 13 represent the phosphates identified in this study. The structures of these compounds are indicated in Table 1. Precise quantitation was not attempted in this screening study, but an approximate concentration of the phosphate represented by the largest peak (peak 5), compared to isotopic internal standards, is 10 ppm. The characteristic ions obtained by EI-MS are shown in Table 2. Several phosphates share many of the same characteristic ions. For example, the  $m/z$  99 ion, which is present for most of the phosphates, is representative of a phosphate moiety,  $\text{H}_4\text{PO}_4$ . Mass-to-charge ratio 125 ( $\text{H}_2\text{PO}_4 \cdot \text{C}_2\text{H}_4$ )<sup>+</sup> is indicative of an ethyl phosphate group, and  $m/z$  139 ( $\text{H}_2\text{PO}_4 \cdot \text{C}_3\text{H}_6$ )<sup>+</sup> of a propyl phosphate. Most phosphates did not show a molecular ion at a significant relative abundance under EI conditions, but it is interesting to note that, when molecular ions for the chlorinated phosphates were observed, the molecular ions were present in a pseudomolecular form,  $[\text{M} + \text{H}]^+$ . This effect has been noted in our laboratory for other chlorinated and oxygenated compounds.

High resolution CI and high resolution EI-MS were crucial in assigning structures; they provided accurate masses, and hence empirical formulae, for each molecular ion and for selected fragments. Accurate CI mass data for the pseudomolecular ions of these 13 compounds are presented in Table 3. GC/FT-IR provided additional structural information from absorbances characteristic of each phosphate structure, confirming many structural characteristics proposed by using mass spectral techniques and also allowing precise structural assignments that would not have been possible with mass spectral techniques alone. Displayed in Figure 1b is the GC/FT-IR chromatogram obtained for this extract; it shows the total absorbance through the entire mid-IR region as a function of retention time and is analogous to the GC/MS total ion current chromatogram. Peaks labeled 1 through 13 correspond to labeled peaks in the GC/MS chromatogram of Figure 1a. Characteristic IR peaks for alkyl phosphates that were observed in the spectra of these 13 compounds include the strong P=O stretching peak at about 1250–1310  $\text{cm}^{-1}$ . This peak was often split as a result of rotational isomerisms. The P—O—C stretching vibrations give rise to several peaks in the 1000–1100  $\text{cm}^{-1}$  region that were the most intense in the spectra. The P—O—C vibrations are complex, involving both in-phase and out-of-phase stretching of the P—O and O—C bonds, thus resulting (in many cases) in several peaks [16].

Structures were assigned to the phosphates by

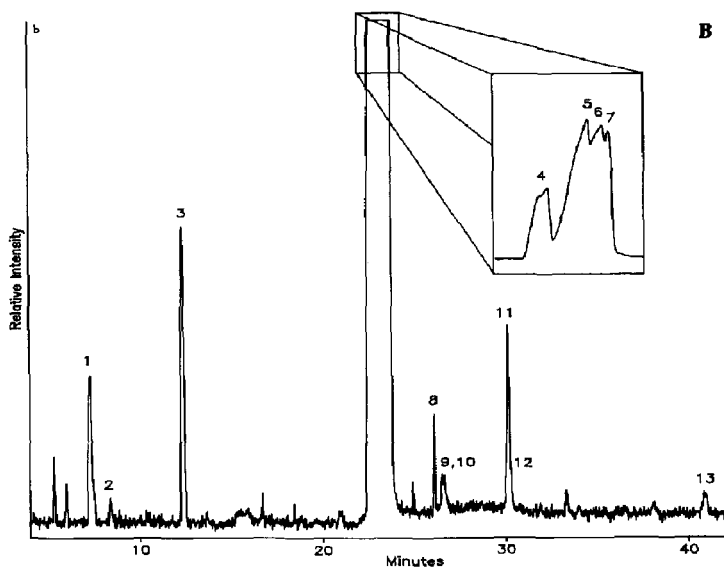
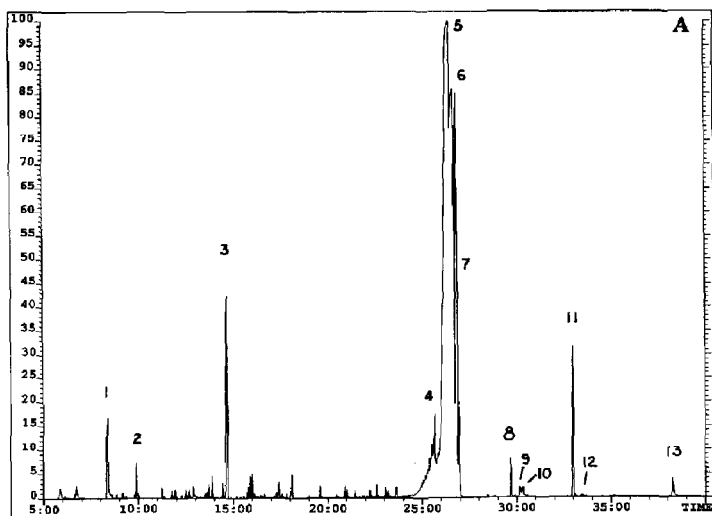


Figure 1. (a) Low resolution GC/MS chromatogram for base/neutral extract and (b) GC/FT-IR chromatogram for base/neutral extract.

using this combination of mass spectral and IR techniques, and they were examined in light of the known chemistry conducted at the fire-retardant chemical plant [4, 17]. To make a variety of fire-retardant chemicals, ethylene oxide, propylene oxide, and epichlorohydrin are each reacted with phosphorus oxychloride to make chloroalkyl phosphates, dichloroalkyl phosphates, and chloroalkyl diphosphates. Some identified compounds were determined to be products manufactured by the plant, and others were either reactants used or byproducts that could be formed.

## Discussion

The mass spectra of the first four GC peaks gave tentative library mass spectrometry data base matches to the following compounds: dimethylmethyl phos-

phonate (compound 1), trimethyl phosphate (compound 2), triethyl phosphate (compound 3), and tris(2-chloroethyl)phosphate (compound 4). High resolution CI-MS and high resolution EI-MS data confirmed these assignments. In addition, GC/FT-IR spectra showed excellent agreement between the sample and IR library spectra for these compounds.

Each of the nine remaining peaks identified in this study gave low resolution EI-MS ions consistent with a chloroalkyl-phosphate structure. Low resolution CI and sometimes low resolution EI were sufficient to determine the number of chlorine atoms present in each compound. However, because none of these remaining phosphates was represented in either the mass spectral or IR library data bases, additional techniques, such as high resolution EI, high resolution CI, and GC/FT-IR were necessary to determine struc-

Table 1. Structures of the 13 compounds discussed in this study

Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1	OCH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>
2	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>
3	OCH <sub>2</sub> CH <sub>3</sub>	OCH <sub>2</sub> CH <sub>3</sub>	OCH <sub>2</sub> CH <sub>3</sub>
4	OCH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> Cl
5	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl
6	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl
7	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl
8	OCH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl
9	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl
10	OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl
11	OCH(CH <sub>2</sub> Cl) <sub>2</sub>	OCH(CH <sub>2</sub> Cl) <sub>2</sub>	OCH(CH <sub>2</sub> Cl) <sub>2</sub>
12	OCH(CH <sub>2</sub> Cl) <sub>2</sub>	OCH(CH <sub>2</sub> Cl) <sub>2</sub>	OCH <sub>2</sub> CHClCH <sub>2</sub> Cl
13	OCH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> Cl	OCH <sub>2</sub> CH <sub>2</sub> OP(O)(OCH <sub>2</sub> CH <sub>2</sub> Cl) <sub>2</sub>

tures. A detailed description of the application of these multispectral techniques to the structural elucidation of these phosphates follows.

As is typical for isomeric compounds, peaks labeled 5, 6, and 7 in Figure 1a exhibited low resolution EI mass spectra with ions of identical mass, but with very different relative abundances. CI-MS showed that the molecular weight of each of the three isomers was 326. High resolution EI and CI data suggested each to be a tris(chloropropyl)phosphate of the general structure (ClC<sub>3</sub>H<sub>6</sub>O)<sub>3</sub>PO. The proposed formation of the pertinent fragment ions for compounds 5, 6, and 7 is shown in Scheme I. Possible exact structures could include either an *n*-propyl or isopropyl arrangement of carbon atoms. No pure commercial standards were available; however, careful interpreta-

tion of mass spectral data provided exact structural assignments. Compound 5 shows an intense ion at *m/z* 277, resulting from a loss of CH<sub>2</sub>Cl, and a weak ion at *m/z* 311 from loss of a methyl group. Taken together, these ions suggest an isopropyl arrangement of carbon atoms, and the loss of CH<sub>2</sub>Cl suggests a terminal location for the chlorine atom on each alkyl chain. Also, because there is no ion at *m/z* 263, hence no loss of CH<sub>2</sub>CH<sub>2</sub>Cl, an isopropyl arrangement for all three alkyl chains is indicated. Therefore, we determine compound 5 to be tris(1-chloro-2-propyl)phosphate.

Chromatographic peaks 6 and 7 required more careful spectral interpretation. Both of their mass spectra contained the *m/z* 263 ion (loss of a CH<sub>2</sub>CH<sub>2</sub>Cl), indicating that at least one of the three

Table 2. Characteristic ions of phosphates

Compound	MW	Characteristic monoisotopic ions (rel. abund.)
1	124	79(91); 94(100); 109(54); 124(33)
2	140	79(40); 95(31); 110(100); 140(25)
3	182	81(57); 99(95); 125(30); 155(100); 182(20)
4	284	63(100); 99(40); 125(31); 187(22); 205(59); 223(42); 235(22); 249(90)
5	326	77(34); 99(96); 125(100); 139(27); 201(54); 215(12); 233(14); 251(10); 277(64); 291(13); 311(1)
6	326	77(25); 99(100); 125(75); 139(30); 201(38); 215(11); 233(17); 251(8); 263(2); 277(42); 291(12); 311(0.5)
7	326	77(10); 99(100); 125(30); 139(25); 201(15); 215(8); 233(4); 251(6); 263(3); 277(16); 291(9); 311(0.1)
8	328	63(100); 99(25); 125(75); 187(35); 249(49); 279(13); 293(7)
9	384	77(14); 99(52); 125(23); 139(100); 201(5); 215(32); 251(7); 264(2); 277(3); 291(14); 321(1); 335(6)
10	384	77(16); 99(46); 125(11); 139(100); 201(2); 215(27); 251(6); 264(5); 277(1); 291(13); 321(3); 335(2)
11	428	75(100); 99(82); 191(74); 209(52); 269(8); 301(23); 319(29); 379(47); 393(2)
12	428	75(100); 99(86); 191(81); 209(48); 269(4); 301(10); 319(19); 379(28); 393(7)
13	470	63(100); 99(30); 125(58); 187(43); 213(98); 249(45); 267(13); 329(9); 391(24); 421(10); 435(14)

**Table 3.** Chemical ionization accurate masses of  $[M + H]^+$  ions

Compound	Empirical formula	Observed mass	Calculated mass
1	C <sub>3</sub> H <sub>10</sub> O <sub>3</sub> P	125.037	125.037
2	C <sub>3</sub> H <sub>10</sub> O <sub>4</sub> P	141.031	141.031
3	C <sub>6</sub> H <sub>16</sub> O <sub>4</sub> P	183.078	183.079
4	C <sub>6</sub> H <sub>13</sub> O <sub>4</sub> PCl <sub>3</sub>	284.962	284.962
5	C <sub>9</sub> H <sub>19</sub> O <sub>4</sub> PCl <sub>3</sub>	327.008	327.009
6	C <sub>9</sub> H <sub>19</sub> O <sub>4</sub> PCl <sub>3</sub>	327.008	327.009
7	C <sub>9</sub> H <sub>19</sub> O <sub>4</sub> PCl <sub>3</sub>	327.008	327.009
8	C <sub>9</sub> H <sub>17</sub> O <sub>5</sub> PCl <sub>3</sub>	328.987	328.988
9	C <sub>12</sub> H <sub>25</sub> O <sub>5</sub> PCl <sub>3</sub>	385.050	385.051
10	C <sub>12</sub> H <sub>25</sub> O <sub>5</sub> PCl <sub>3</sub>	385.050	385.051
11	C <sub>9</sub> H <sub>18</sub> O <sub>4</sub> PCl <sub>6</sub>	428.891	428.892
12	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub> PCl <sub>6</sub>	428.891	428.892
13	C <sub>10</sub> H <sub>21</sub> O <sub>6</sub> P <sub>2</sub> Cl <sub>4</sub>	470.947	470.944

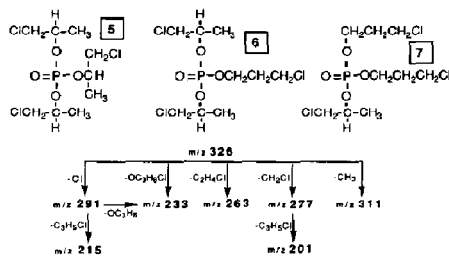
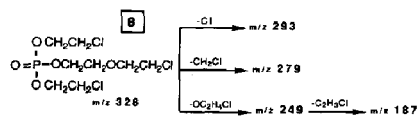
chloroalkyl chains was an *n*-propyl chain for both compounds. Also, both compounds exhibited the  $m/z$  277 and  $m/z$  311 ions (losses of CH<sub>2</sub>Cl and CH<sub>3</sub>) in their spectra, again suggesting some isopropyl arrangement in the structure. Because peak 6 showed a comparatively abundant ion due to loss of CH<sub>2</sub>Cl ( $m/z$  277), indicating a branching point, two isopropyl chains are likely for this structure. The mass spectrum also looks very similar in many respects to the spectrum of compound 5, which has three isopropyl chains in its structure. Therefore, we assign peak 6 as bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate (compound 6). The comparatively low abundance of the  $m/z$  277 ion (loss of CH<sub>2</sub>Cl) and the comparatively abundant ion due to loss of CH<sub>2</sub>CH<sub>2</sub>Cl ( $m/z$  263) support the assignment of peak 7 as bis(3-chloro-1-propyl)(1-chloro-2-propyl)phosphate (compound 7).

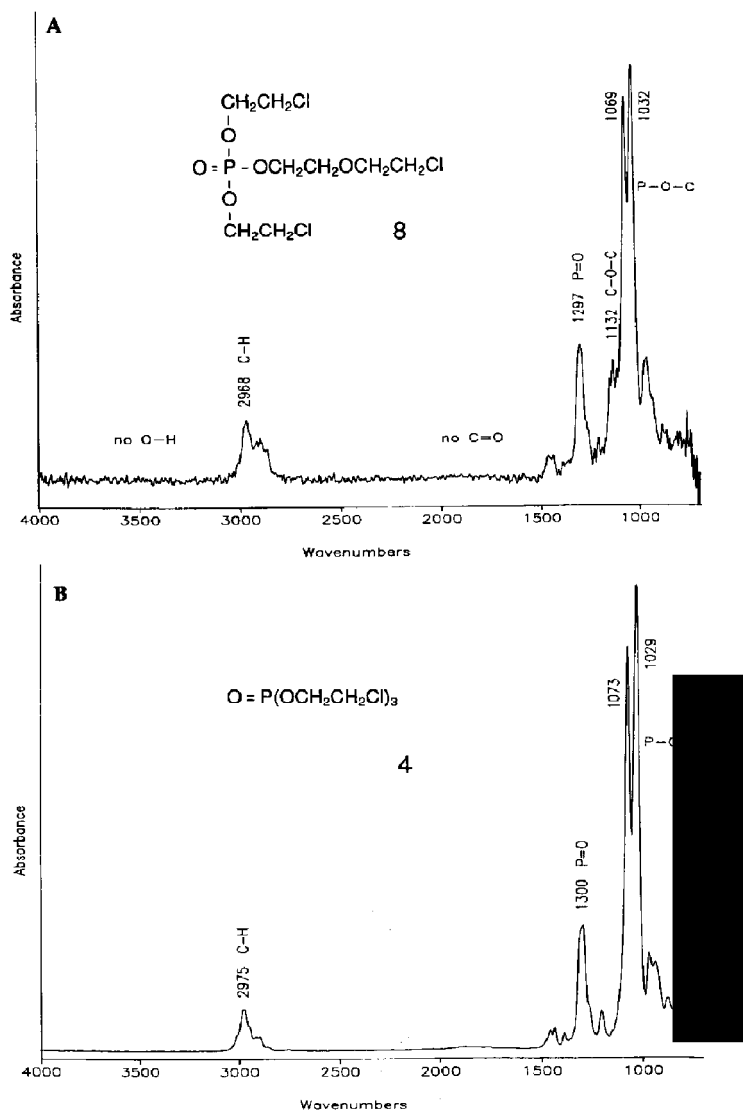
The assignments for peaks 5, 6, and 7 are supported also by GC retention times, as compounds with branched-chain structures typically are eluted earlier than straight-chain structures on a low polarity GC column such as DB-5 [18]. The IR spectroscopic data for peaks 5, 6, and 7 (P=O stretching peak frequencies of 1303/1292 cm<sup>-1</sup>, 1300/1283 cm<sup>-1</sup>, and 1304/1288 cm<sup>-1</sup>, respectively, and P-O-C stretching peak frequencies of 1071/1020 cm<sup>-1</sup>, 1045/1005

cm<sup>-1</sup>, and 1032/1010 cm<sup>-1</sup>, respectively) agreed with the general alkyl phosphate structures and was consistent with the exact structures proposed by mass spectrometry.

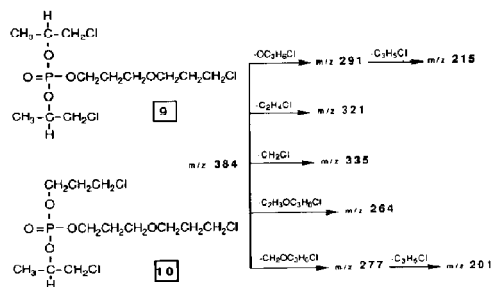
The low resolution mass spectrum of the chromatographic peak labeled 8 exhibited many of the same ions seen in the mass spectrum of tris(2-chloroethyl)phosphate (compound 4), indicating that it was a phosphate with a similar structure. However, this compound showed a molecular weight of 328 by CI-MS. It was found by high resolution CI to contain an additional oxygen atom and to have an empirical formula of C<sub>8</sub>H<sub>16</sub>O<sub>5</sub>Cl<sub>3</sub>P. As shown in Scheme II, there were three primary scissions evident from the EI spectrum for compound 8: the loss of Cl, CH<sub>2</sub>Cl, and OC<sub>2</sub>H<sub>4</sub>Cl. Infrared spectroscopy provided the remaining necessary pieces of information. The additional oxygen atom would most likely be present as an ether, a carbonyl, or an alcohol functionality. There was no indication in the IR spectrum of either C=O or O-H stretching peaks (both of which are easily detected in the IR at about 1650-1850 cm<sup>-1</sup> and 3500-3700 cm<sup>-1</sup>, respectively). Unlike OH and C=O, ether linkages, which absorb at about 1100 cm<sup>-1</sup>, cannot always be unequivocally assigned due to absorbances of many other vibrations in this region. Also in comparing the IR spectrum of peak 8 to that of compound 4, we observed a shoulder on the intense P-O-C stretching peak at about 1135 cm<sup>-1</sup> for peak 8, which is not present in the spectrum of compound 4, as shown in Figure 2. This indicates the presence of an ether linkage in the structure of the peak 8 compound. However, in light of the empirical formula provided by high resolution mass spectrometry, the most conclusive evidence for ether linkage in this structure is the absence of OH and C=O IR absorbances. The high resolution mass spectrometry and IR data, coupled with the similarity of the low resolution mass spectrum and IR spectrum to that of tris(2-chloroethyl)phosphate, indicate the compound is bis(2-chloroethyl)-2-(2-chloroethoxy)ethyl phosphate (compound 8).

Peaks 9 and 10 are also isomers of each other, as evidenced by similar low resolution EI mass spectra. Each compound revealed a molecular weight of 384 by CI, and an empirical formula of C<sub>12</sub>H<sub>24</sub>O<sub>5</sub>Cl<sub>3</sub>P by high resolution CI. The formation of the pertinent fragment ions for compounds 9 and 10 is shown in Scheme III. Further aiding in structural assignments, the low resolution EI mass spectra of peaks 9 and 10 showed many of the same low mass ions and losses of C<sub>3</sub>H<sub>5</sub>Cl evident in the mass spectra of compounds

**Scheme I****Scheme II**



**Figure 2.** Infrared spectrum of (a) bis(2-chloroethyl)-2-(2-chloroethoxy)ethyl phosphate (compound 8) and (b) tris(2-chloroethyl)phosphate (compound 4).



**Scheme III**

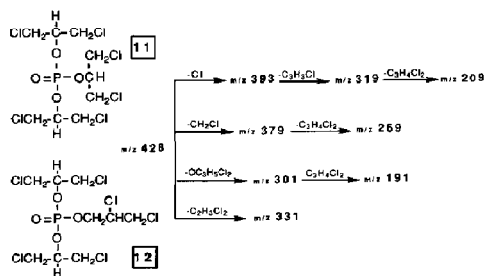
5, 6, and 7 that were indicative of chloropropyl chains in the chemical structure. This comparison, analogous to the comparison made between compound 4, tris(2-chloroethyl)phosphate, and compound 8, bis(2-chloroethyl)-2-(2-chloroethoxy)ethyl phosphate, suggests that the primary structural difference between the compounds represented by peaks 9 and 10 and compounds 5, 6, and 7 might be an additional propyl ether linkage. Infrared spectroscopy provided evidence to support this proposal. As was true for compound 8, GC/FT-IR gave no evidence of an OH or a C=O absorbance, indicating that the fifth oxygen was present in an ether linkage. Furthermore (as with the spectrum of compound 8), the IR spectra of peaks 9 and 10 have shoulders on the intense P-O-C

stretching peaks (at about  $1125\text{ cm}^{-1}$ ), probably due to the C—O—C stretching vibration. Therefore, the general structure  $(\text{ClC}_2\text{H}_4\text{O})_2\text{P}(\text{O})(\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{Cl})$  was likely.

Assigning specific structures to the two isomers required further spectral interpretation, as no pure standards with this empirical formula could be purchased. For peak 9, both low and high resolution EI-MS revealed key fragments to aid in the structural elucidation. Among the important fragments were losses of  $\text{CH}_2\text{Cl}$  ( $m/z$  335) and  $\text{CH}_2\text{CH}_2\text{Cl}$  ( $m/z$  321). The comparatively abundant  $m/z$  335 ion (loss of  $\text{CH}_2\text{Cl}$ ) for peak 9 indicates a branching point, suggestive of an isopropyl chain and, therefore, more isopropyl character to the structure. The low abundance  $m/z$  321 ion (a loss of  $\text{CH}_2\text{CH}_2\text{Cl}$ ) indicates at least one *n*-propyl group in the structure, and the ion at  $m/z$  264 (a neutral loss of  $\text{C}_2\text{H}_3\text{OC}_3\text{H}_6\text{Cl}$ ) suggests that the internal propoxy linkage has an *n*-propyl arrangement. Therefore, peak 9 was identified as bis(1-chloro-2-propyl)-3-(3-chloropropoxy)propyl phosphate (compound 9).

Again, comparing the spectra of peaks 9 and 10, the comparatively abundant  $m/z$  321 ion (loss of  $\text{CH}_2\text{CH}_2\text{Cl}$ ) for peak 10 suggests two *n*-propyl groups, and the comparatively low abundance of the  $m/z$  335 ion (loss of  $\text{CH}_2\text{Cl}$ ) suggests a single isopropyl group. As for compound 9, the ion at  $m/z$  264 suggests the internal propoxy linkage has an *n*-propyl arrangement. The identification of peak 10 as (1-chloro-2-propyl)(3-chloro-1-propyl)-3-(3-chloro-1-propoxy)propyl phosphate (compound 10) would be consistent with all data obtained.

The next two chromatographic peaks, 11 and 12, also displayed mass spectra indicative of isomers with chloroalkyl phosphate structures. Chemical ionization revealed the molecular weight of each phosphate to be 428. High resolution CI yielded an empirical formula of  $\text{C}_9\text{H}_{15}\text{O}_4\text{Cl}_6\text{P}$  for each. The formation of the pertinent fragment ions for compounds 11 and 12 is shown in Scheme IV. These data, along with fragment information provided by low resolution EI-MS, suggest a general tris(dichloropropyl)phosphate structure for each. For peak 11, isopropyl groups are indicated because there was no loss of  $\text{C}_2\text{H}_4\text{Cl}$ . Also,

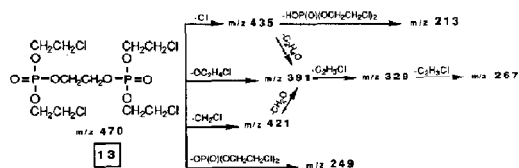


Scheme IV

there was a very abundant ion due to loss of  $\text{CH}_2\text{Cl}$  ( $m/z$  379), indicating a branching point. Therefore, peak 11 was identified as tris(1,3-dichloro-2-propyl)phosphate (compound 11). This particular compound is a commonly used flame retardant and was obtained commercially. The mass and IR spectra and GC retention time of peak 11 matched those of the standard exactly, confirming our structural assignment.

The mass spectrum of peak 12 closely resembled the spectrum for compound 11. Minor differences included the presence of the  $m/z$  331 ion due to loss of  $\text{C}_2\text{H}_3\text{Cl}_2$ , a more abundant ion at  $m/z$  393 due to loss of  $\text{Cl}$ , and a somewhat less abundant  $m/z$  379 ion due to loss of  $\text{CH}_2\text{Cl}$ . All of these are reasonable for a structure with both isopropyl and *n*-propyl substituents. The fire-retardant synthesis at the plant [4, 17] involves the reaction of epichlorohydrin and phosphorus oxychloride. This reaction produces primarily 1,3-dichloro-2-propyl substitution with a lesser amount of 2,3-dichloro-1-propyl substitution. In light of this chemistry, the structure assigned to peak 12 is bis(1,3-dichloro-2-propyl)(2,3-dichloro-1-propyl)phosphate (compound 12).

The chromatographic peak labeled 13 revealed a molecular weight of 470 by CI, and an empirical formula of  $\text{C}_{10}\text{H}_{20}\text{O}_8\text{Cl}_4\text{P}_2$ . By low resolution EI, the lower half of the mass spectrum looked very similar to that seen for tris(2-chloroethyl)phosphate (compound 4), suggesting that compound 13 is a dimeric phosphate related to compound 4. Furthermore, the IR spectrum of this compound was virtually identical to that of compound 4. Scheme V shows the formation of pertinent mass spectral fragments for compound 13. The mass spectrum of this compound showed a significant ion at  $m/z$  391 (loss of  $\text{OC}_2\text{H}_4\text{Cl}$ ), indicating a general chloroethylphosphate structure. Additional mass spectral data support the exact structure shown in Scheme V. First,  $m/z$  249 (a loss of  $\text{OP}(\text{O})(\text{OCH}_2\text{CH}_2\text{Cl})_2$ ) could be represented by cleavage of the C—O bond from the central ethylene group. The abundant ion at  $m/z$  213 arises from the loss of  $\text{HOP}(\text{O})(\text{OCH}_2\text{CH}_2\text{Cl})_2$  from the  $m/z$  435 ion. Thus, peak 13 was identified as 1,2-bis[bis(2-chloroethyl)phosphato]ethane (compound 13). This compound is a commercial fire retardant and a sample was obtained. The GC retention time, mass, and IR spectra were identical for the standard and the compound representing peak 13.



Scheme V

## Conclusions

By using a multispectral analysis approach, we identified 13 alkyl and chloroalkyl phosphates in a sample effluent taken from a plant that manufactures fire-retardant chemicals. Of these 13 phosphates, bis(2-chloroethyl)-2-(2-chloroethoxy)ethyl phosphate (compound 8), bis(1-chloro-2-propyl)-3-(3-chloropropoxy)propyl phosphate (compound 9), and (1-chloro-2-propyl)(3-chloro-1-propyl)-3-(3-chloro-1-propoxy)propyl phosphate (compound 10) exhibited chemical structures different from those of the commercially manufactured fire retardants and the reactants used in their synthesis. Occurrence of these compounds is reasonable based on the known chemistry of the synthesis process used in manufacture of fire retardants [4]. One compound we identified, tris(1,3-dichloro-2-propyl)phosphate (compound 11), is known to be mutagenic [19]. As most of the chlorophosphates we identified are structurally similar, the fact that one of them is a known mutagen suggests the consideration of additional toxicity/mutagenicity studies. Multispectral techniques provided information necessary to define the exact structures of these phosphates. As these examples show, low resolution GC/MS alone does not always provide all information necessary for absolute structural assignments and, therefore, multispectral techniques may be necessary to identify precisely organic compounds in complex environmental samples.

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## References

1. Midwest Research Institute, Draft Final Report, 1979, EPA Contract No. 68-01-4313.
2. Sanders, H. J. *Chem. and Eng. News* 1978, April 24, 22-36.
3. Hudec, T.; Thean, J.; Kuehl, D.; Dougherty, R. C. *Science* 1981, 211, 951-952.
4. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 10; Standen, A., Ed.; Wiley: New York, 1980; pp 401-416.
5. Modern Plastics: Special Report. *Modern Plastics* 1985, 62, September, 63-65.
6. Rostad, C. E.; Pereira, W. E.; Leiker, T. J. *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, May 1989; pp 1433-1434.
7. Thruston, A. D., Jr. *J. Chromatogr. Sci.* 1978, 16, 254-259.
8. Ishikawa, S.; Taketomi, M.; Shinohara, R. *Water Res.* 1985, 19, 119-125.
9. Williams, D. T.; LeBel G. L. *Bull. Environ. Contam. Toxicol.* 1981, 27, 450-457.
10. Blum, A.; Ames, B. N. *Science* 1977, 195, 17-22.
11. Blum, A.; Gold, M. D.; Ames, B. N.; Kenyon, C.; Jones, F. R.; Hett, E. A.; Dougherty, R. C.; Horning, E. C.; Dzidic, I.; Carroll, D. I.; Stillwell, R. N.; Thenot, J.-P. *Science* 1978, 201, 1020-1023.
12. Ulsamer, A. G.; Porter, W. K.; Osterberg, R. E. *J. Environ. Pathol. Toxicol.* 1978, 1, 543-549.
13. Gutenmann, W. H.; Lisk, D. J. *Bull. Environ. Contam. Toxicol.* 1975, 14, 61.
14. Maylin, G. A.; Henion, J. D.; Hicks, L. J.; Leibovitz, L.; Ahrens, V. D.; Gilbert, M.; Lisk, D. J. *Bull. Environ. Contam. Toxicol.* 1977, 17, 499-504.
15. *Federal Register*. 1984, 49, 43234.
16. Nyquist, R. A.; Potts, W. J., Jr. In *Analytical Chemistry of Phosphorous Compounds*, Halmann, M., Ed.; Wiley-Interscience: New York, 1972; pp 189-293.
17. Wise, H. E., Jr. Personal Communication. Industrial Technology Division, Office of Water, U.S. Environmental Protection Agency, 1990.
18. *The Sadtler Standard Gas Chromatography Retention Index Library*, Sadtler Research Laboratories, Philadelphia, PA, 1985.
19. Gold, M. D.; Blum, A.; Ames, B. N. *Science* 1978, 200, 785-787.