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DETERMINATION OF ORGANOPHOSPHORIC AND ORGANOPHOSPHOROTHIOIC ACIDS IN AQUEOUS SOLUTIONS BY ION CHROMATOGRAPHY

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SUMMARY

An ion chromatographic procedure is described for the separation and determination of methyl and ethyl phosphates, phosphorothioates and phosphoric acid in aqueous solutions at the part per million level. The separations are achieved on columns of low capacity anion-exchange resin with sodium carbonate–bicarbonate eluent. Detection is accomplished by a combination of conductivity and UV absorbance at 210 nm. The UV detector gives more specificity and sensitivity for organophosphorothioates, while discriminating against a strong chloride interference with the conductimetric detection of the dialkylated organophosphorothioic acids.

INTRODUCTION

In the past gas chromatographic (GC) methods for measurement of organophosphoric and organophosphorothioic acids in waste brines and foodstuffs[1] have been employed. The acids must be isolated from the water and derivatized with diazomethane before analysis, however. Thin-layer chromatography (TLC) has also been a popular technique for determining the acids[2–4] but it suffers from many disadvantages, non-quantitative results, extraction is required and difficulties with visualization of the developed TLC plate.

Recently an ion chromatographic determination of dibutylphosphate in water was reported[5]. We also were inspired by the development of ion chromatography and achieved an ion chromatographic procedure for determining the methyl and ethyl phosphates and phosphorothioates in water. However, the major components of interest, diethylphosphorothioic acid (DEPT) and dimethylphosphorothioic acid (DMPT) were obscured by chloride in the samples of interest.

Since organophosphates are not detectable by UV absorption it was decided to retain the conductivity detector for this determination and to add a UV detector to the conductivity cell outlet. This would take advantage of the strong UV absorption properties of the phosphorothioic acids and discriminate against the chloride interference.

EXPERIMENTAL

Apparatus

A schematic of the analytical system used is shown in Fig. 1. Three 300 × 2.8 mm glass columns packed with a low-capacity anion-exchange resin agglomerated on 180–230 mesh surface-sulfonated styrene divinyl benzene, 0.011 mequiv./g capacity were used. One 300 × 2.8 mm glass column, packed with Dowex AG 50W-X16 high-capacity cation-exchange resin, 200–400 mesh in the hydrogen form was employed. Sodium carbonate–sodium bicarbonate, 0.0012 *M* each in distilled deionized water at 1.0 ml/min flow-rate was used as eluent. A Modern Metalcraft BM-2 conductivity cell and a Perkin-Elmer LC-55 UV detector at 210 nm were used.

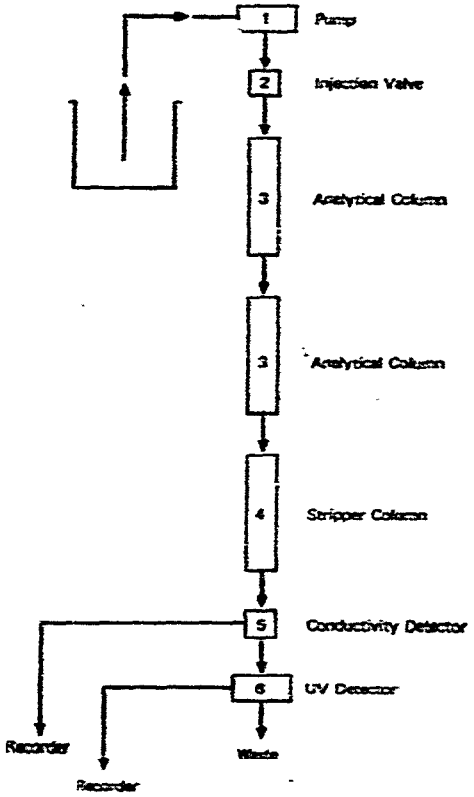

Fig. 1. Schematic diagram of apparatus.

The sample size was 170 μl. A small 100 × 2.8 mm glass column packed with cation-exchange resin was connected to the outlet of the analytical system to eliminate bubble formation from the carbonic acid in the eluent.

Reagents

Analytical-grade sodium carbonate and sodium bicarbonate were used to prepare the mobile phase. For regeneration of the stripping column, 1.0 *N* reagent-

grade nitric acid was used. The stripper was regenerated for about 20 min and then washed with deionized water until the column effluent was neutral (≈ 15 min).

Standards

The standards and other reagents used, when commercially available, were technical grade or better. Three, however, were prepared in the Agricultural Synthesis Group at Dow. They were potassium O,O-diethylphosphate (KDEP), potassium O,O-diethylphosphorothioate (KDEPT) and potassium O,O-dimethylphosphorothioate (KDMPT). They were analysed by phosphorus ^{31}P nuclear magnetic resonance (NMR) and by infrared (IR) spectrometry for impurities and verification of structure. All three standards showed traces of water by IR, but only in the case of KDMPT was any other impurity detected. From the NMR spectrum the KDMPT standard appears to contain about 4% of what is suspected to be O-methyl-O-ethylphosphorothioate. The monoethylphosphoric (MEP) and monomethylphosphoroic (MMP) acids were obtained commercially and found by titration with standard base and by NMR to be mixtures of roughly equal concentrations of the corresponding mono- and disubstituted organophosphoric acids. The structures of the compounds of interest are shown in Fig. 2.

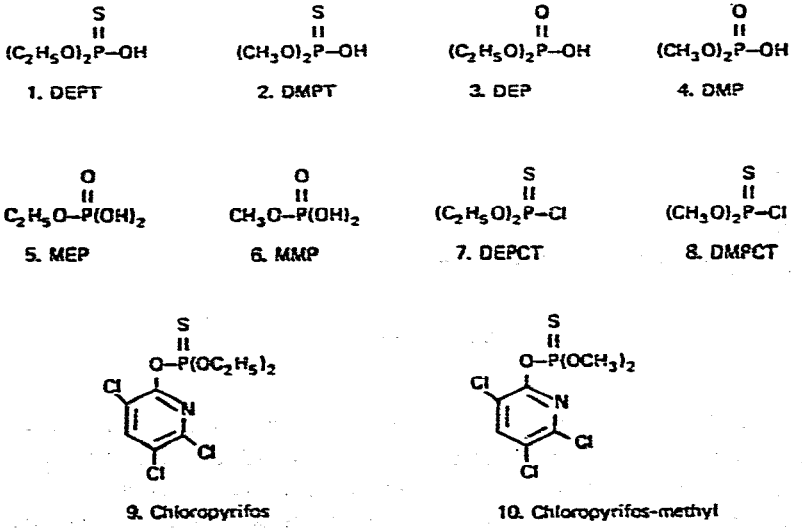

Fig. 2. Structures of components.

RESULTS AND DISCUSSION

In the original work three separating columns of an anion-exchange resin prepared in our laboratories were used. In a later work, analysis of chloropyrifos-methyl, a Dow product, was performed using only one separating column obtained from Dionex (Sunnyvale, Calif., U.S.A.). The obtained separations were comparable to those obtained in the original work. However retention times with the Dionex column were much shorter. Chloride still proved to be a major interference for the detection of DEPT and DMPT by conductivity and the UV detector was required.

Fig. 3 is a UV spectrum of KDEPT in water, obtained with a Cary 17 spectrophotometer. From the spectrum the 210 nm operating wavelength for the UV detector was chosen.

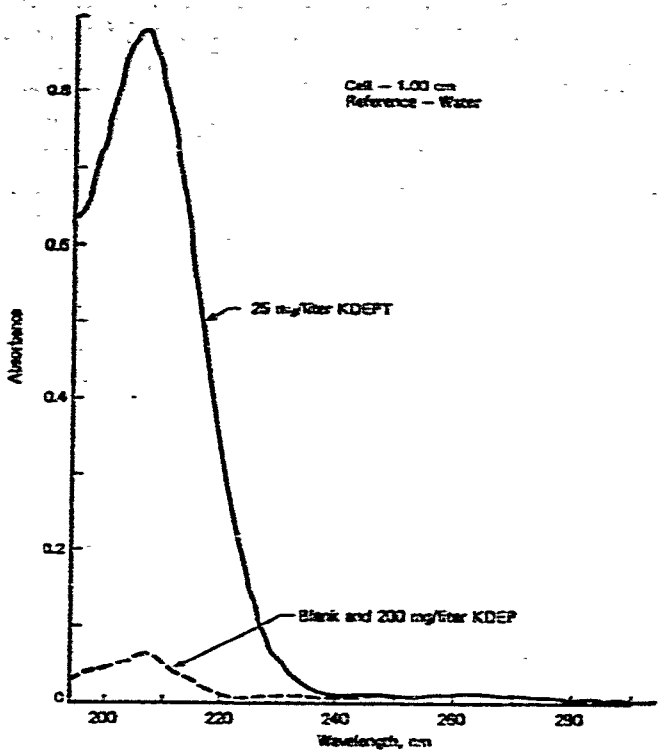

Fig. 3. UV absorption spectrum of potassium O,O-diethylphosphorothioate.

In Figs. 4 and 5 the dual chromatograms for the ethyl and methyl substituted phosphorus species are shown. Chloride at 2.5 ppm has been added in one case to demonstrate the interference observed for the phosphorothioic acids using the conductivity cell response. The eluent strength was chosen as a compromise between short retention times for disubstituted phosphates and long retention times for monosubstituted phosphates.

When water is injected into the system a negative response results near the void volume of the column, and hence near the elution time of the disubstituted phosphates. This makes quantitation for them difficult. The negative peak is the result of a momentary decrease in the carbonic acid concentration in the eluent, and can be eliminated by preparing the standards in the eluent or by adding to carbonate free water samples 1.0% of 100-fold concentrated eluent. Table I lists the estimated detection limits that would have given signal-to-noise ratio of 2.5 on the day the particular standards were run. By optimizing the elution times for anyone particular species, better detection limits could be achieved.

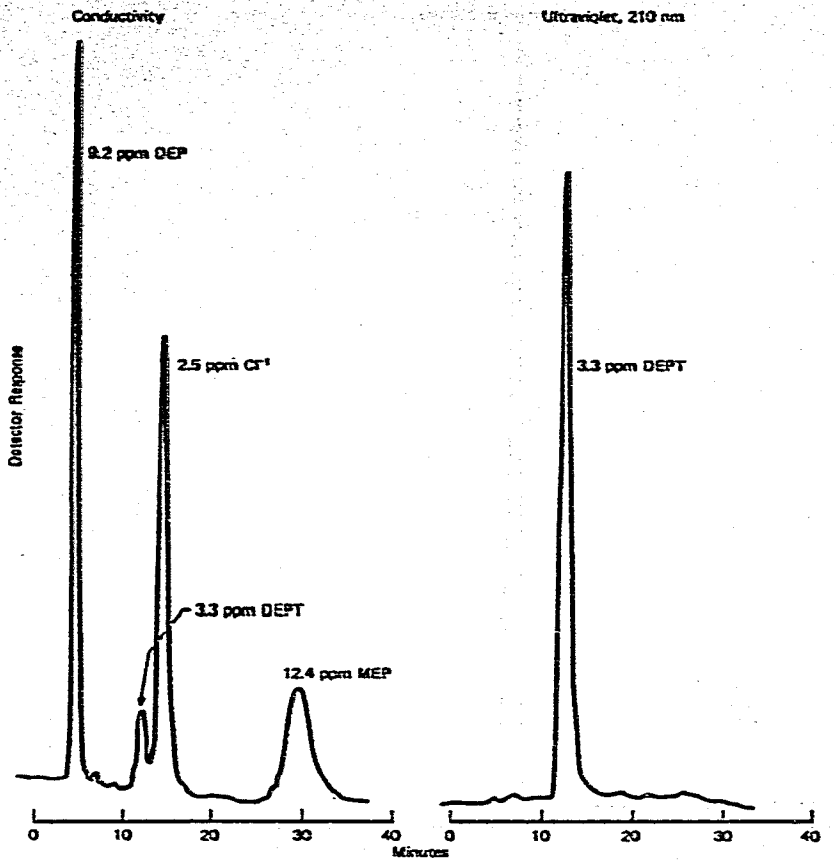

Fig. 4. Dual detector chromatograms of ethyl substituted phosphorus species.

TABLE I

ESTIMATED DETECTION LIMITS

Signal-to-noise ratio, 2.5.

Compound	*Detector*	
	Conductivity (mg/l)	*UV 210 nm (mg/l)*
Diethylphosphate	0.6	—
Dimethylphosphate	0.4	—
Diethylphosphorothioate	0.9	0.2
Dimethylphosphorothioate	0.9	0.2
Diethylphosphate	2.2	—
Monoethylphosphate	1.6	—

Table II lists the retention times and capacity factors for the organophosphorus species tested and for some typical compounds that could be expected in water samples. It is not possible to separate adequately the mono- and dimethylphosphates

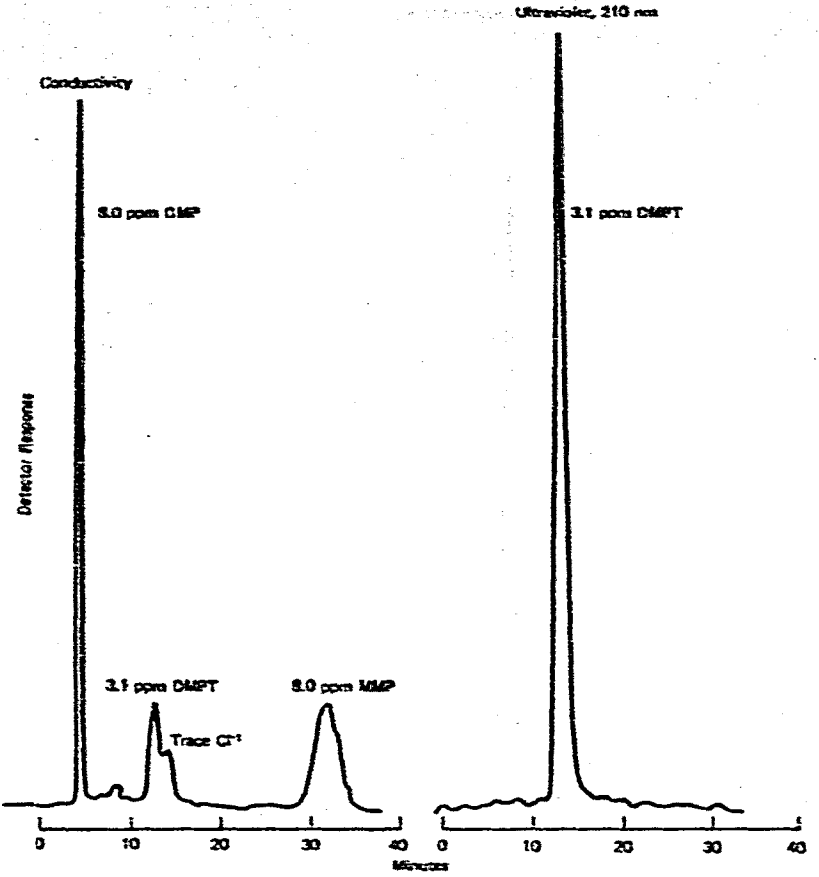

Fig. 5. Dual detector chromatograms of methyl substituted phosphorus species.

TABLE II

ELUTION TIMES FOR ORGANOPHOSPHATES, PHOSPHOROTHIOATES AND SOME POTENTIAL INTERFERENTS

Compound	*Elution time (min)*	*Capacity factor*	*UV response*
Diethylphosphate	4.4	0.1	No
Dimethylphosphate	4.4	0.1	No
Acetate	5.4	0.4	Yes
Glycolate	5.4	0.4	Yes
Formate	6.3	0.7	Yes
Monochloroacetate	8.8	1.3	Yes
Diethylphosphorothioate	11.8	2.1	Yes
Dimethylphosphorothioate	12.5	2.3	Yes
Chloride	14.0	2.7	No
Dichloroacetate	23	5.0	Yes
Monoethylphosphate	28	6.3	No
Monomethylphosphate	31	7.1	No
Nitrate	≈46	11	—
Orthophosphate	>60	>15	No
Sulfate	>60	>15	No

from their corresponding ethyl phosphates, but when all are present at similar levels the peaks are noticeably broadened indicating more than one species.

Fig. 6 shows the standard curves (peak height *versus* concentration) for monoethylphosphate, diethylphosphate and diethylphosphorothioate, using the conductivity cell response. Excellent linearity over the relatively narrow concentration range was observed. The UV responses for the phosphorothioic acids were linear also and would be expected to remain so over a much broader concentration range. The conductivity response, however, is generally more concentration dependent and would have to be tested before analyzing more concentrated samples.

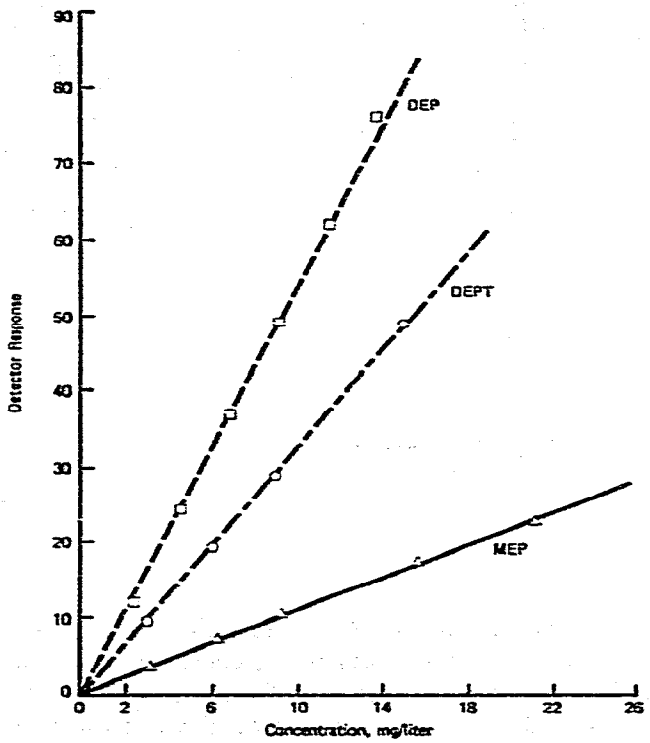

Fig. 6. Standard curves for conductivity detector.

Applications

Organophosphates in waste brines. Organophosphates were determined by the procedure described in this paper in waste brines without any sample preparation. Fig. 7 is a chromatogram of a 250-fold diluted composite brine stream sample from several plants. The conductivity cell response indicates the presence of about 6 ppm DEP and the UV response for DEPT corresponds to 5 ppm in the diluted sample. Improved accuracy of the DEP result could be done using a more dilute eluent if needed.

Hydrolysis rates for diethylphosphorochloridothioate (DEPCT) and dimethylphosphorochloridothioate (DMPCT). The rates of formation of DEPT and chloride

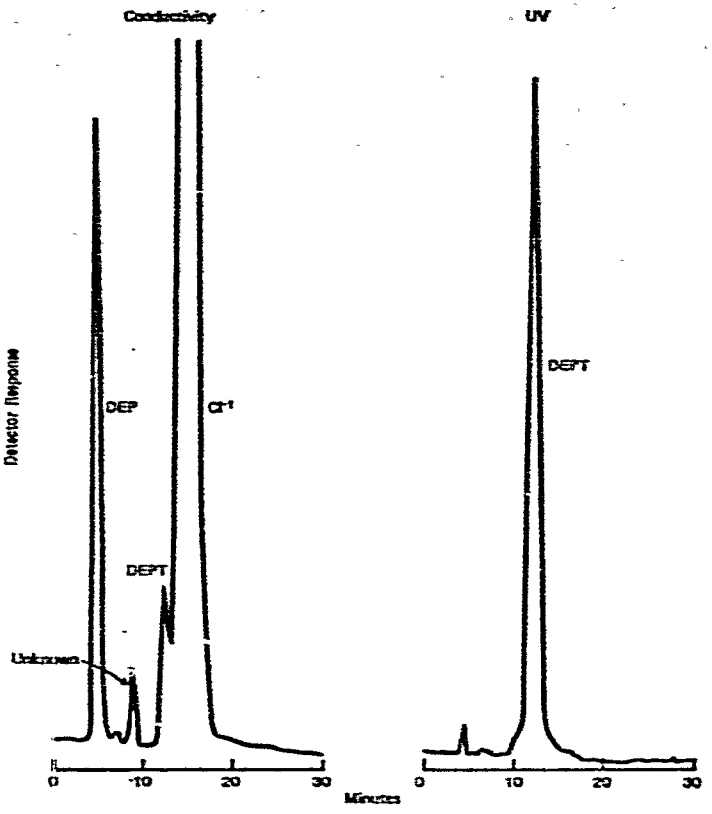

Fig. 7. DEPT in waste brine stream.

ion from DEPCT and DMPT plus chloride from DMPCT were followed using the ion chromatographic system with combined UV and conductivity detection. A 4–6-μl volume of the compound to be studied was injected into a minimum amount of dry acetonitrile, and the mixture was quickly diluted with water or a weak base to 100 ml. Samples were then periodically withdrawn and analyzed. Fig. 8 shows one set of the chromatograms obtained in this study, and the resulting formation curves for DEPT in water and in the mobile phase are plotted in Fig. 9. As can be seen the compound hydrolyzed very fast in water and faster in the eluent, so the results are not totally accurate. A better technique for this study would be to quench the reaction at about 5-min intervals with a hexane or isooctane extraction to remove the unreacted DEPCT from the water. Then each extracted water sample could be analyzed with no time dependence for the analysis. Nevertheless the study demonstrates the ease for determining the reaction rates and the products formed when phosphorus compounds such as pesticides are hydrolyzed.

Organophosphorus acids in production chloropyrifos. The levels of the organophosphorus acids were determined in production chloropyrifos after they were extracted with deionized water from a carbon tetrachloride solution. A 500 × 3 mm

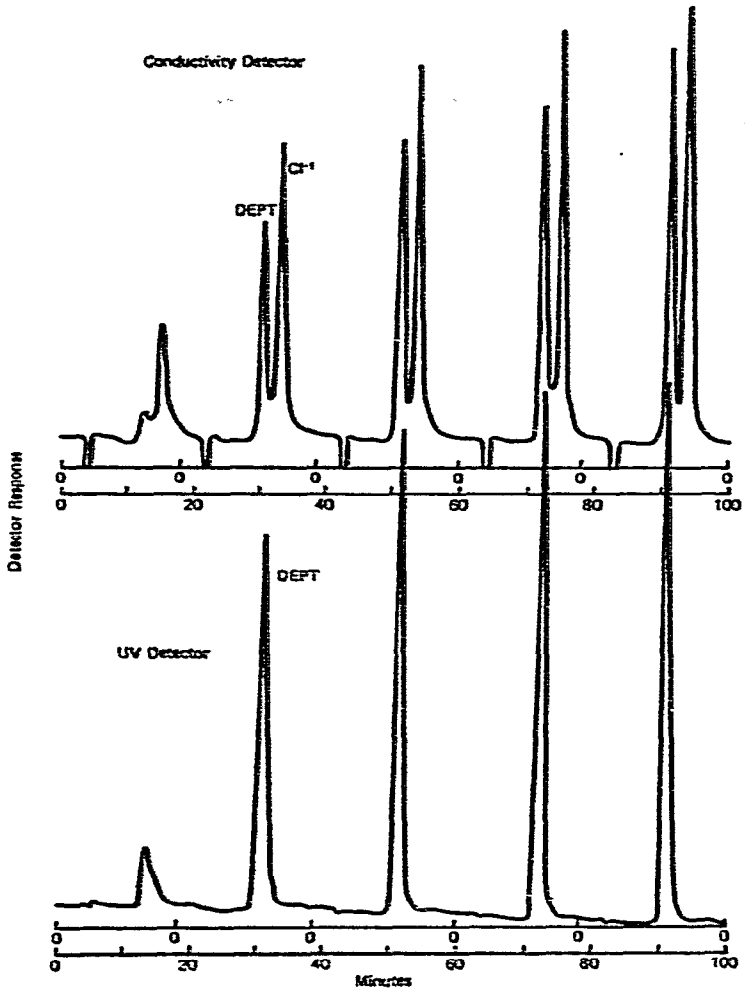

Fig. 8. Chromatograms of DEPCT hydrolysis study.

separating column and a 250 × 6 mm suppressor column both available from Dionex were used.

Extraction procedure

A 2-g amount of sample was dissolved in 10 ml of carbon tetrachloride and then extracted with 20 ml of deionized water for 5 min on a mechanical shaker. After the phases separated (≈1 min), 5 ml of the water layer was filtered into a pre-washed vial using a Swinney filter holder and 5.0 μm Mitex (PTFE) Millipore filter. The filtered water was again extracted with 5 ml carbon tetrachloride for 1 min, 50 μl of 100-fold concentrated eluent (0.10 *M* Na_2CO_3 + 0.1 *M* $NaHCO_3$) was added, and then the water phase was removed for subsequent analysis.

Deionized water rather than the eluent was used as extracting solvent to decrease any possible slow hydrolysis of chloropyrifos which may occur in a basic

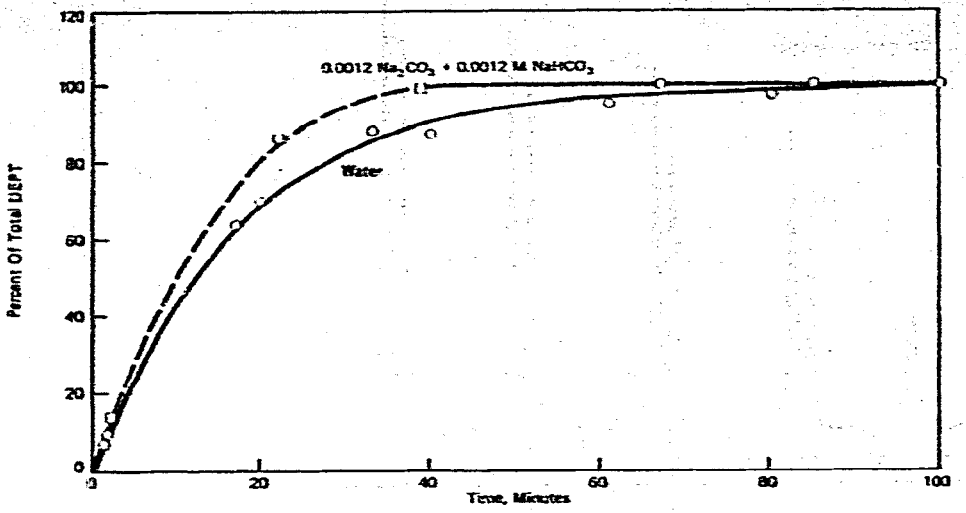

Fig. 9. Hydrolysis of DEPCT to DEPT in water.

solution. The effect of the extraction time on the recovery of methyl phosphorus compounds was evaluated. Known amounts of each compound were added into purified chloropyrifos-methyl dissolved in carbon tetrachloride. Then 5- and 10-min extractions with deionized water and carbonate–bicarbonate solution were performed. The resulting data listed in Table III indicates very good recoveries using water or the eluent as extracting solvent. However, quantitation of DMP was impossible due to the interference by an unknown. Another unknown detectable with both detectors and which was identified as bromide did not interfere with any of the species of interest. Fig. 10 shows dual detector chromatograms of methyl substituted phosphorus species, phosphoric acid and bromide.

TABLE III

RECOVERY STUDY OF ORGANOPHOSPHORIC ACIDS

Sample	*Extraction*		*DMPT*			*MMP*			PO_4^{3-}		
	Solvent	*Min*	*ppm added*	*ppm found*	*Recovery (%)*	*ppm added*	*ppm found*	*Recovery (%)*	*ppm added*	*ppm found*	*Recovery (%)*
Purified chloropyrifos-methyl	Eluent	5	1.97	1.9	94	1.25	1.2	96	7.16	7.3	102
Purified chloropyrifos-methyl	Eluent	5	3.94	3.9	99	2.50	2.5	100	14.32	14.1	98
Purified chloropyrifos-methyl	Eluent	5	3.94	3.9	99	3.75	3.7	99	21.50	20.5	95
Purified chloropyrifos-methyl	Water	5	3.44	3.4	99	—	—	—	—	—	—
Purified chloropyrifos-methyl	Water	10	3.44	3.4	99	—	—	—	—	—	—

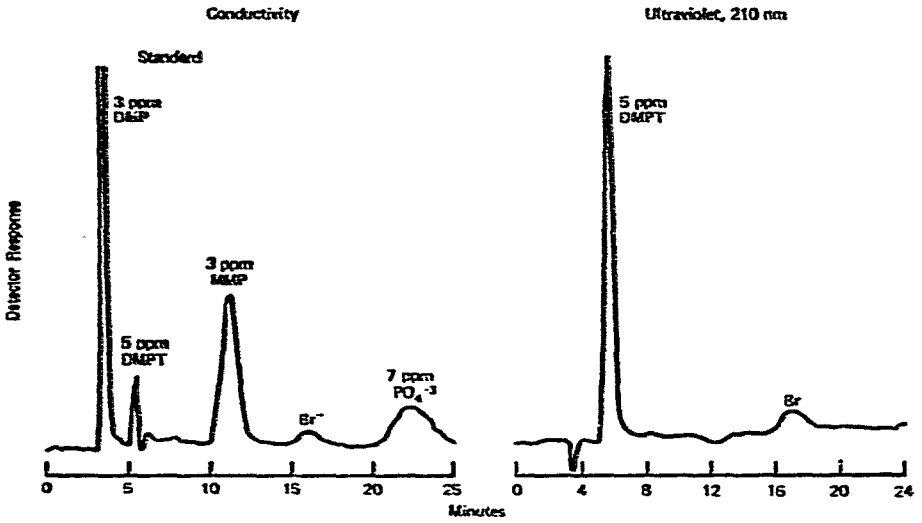

Fig. 10. Dual detector chromatograms of methyl substituted phosphorus species and phosphoric acid.

CONCLUSIONS

The ion chromatographic technique described provides the best truly quantitative procedure for conveniently measuring trace organophosphoric acids in water. Addition of the UV detector to the analytical system permits the simultaneous measurement of UV absorbing phosphorus compounds with the non-absorbing phosphates.

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