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Reference Methods and Materials

Determination of selected organophosporous contaminants in estuarine and coastal water.

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CONTENTS

INTRODUCTION

Organophosphorous (OP) compounds consist of a group of roughly 250 chemicals manufactured all over the world. Approximately 140 of these compounds are pesticides, and the remaining are mainly industrial chemicals used as flame retardants, plasticizers and industrial hydraulic fluids and solvents.

Annex 1 summarizes some of the OP pesticides. They are commonly used worldwide in agriculture or animal husbandry for crop protection and/or elimination of ectoparasites to substitute the persistent organochlorine pesticides which are currently restricted. Generally, the OP insecticides are compounds more toxic for the mammals and less toxic for the fishes (Ramade, 1977). They are also more specific than the organochlorine (Galgani et al, 1990), and they are considered to be less persistent and lipofilic (Schimmel et al, 1983).

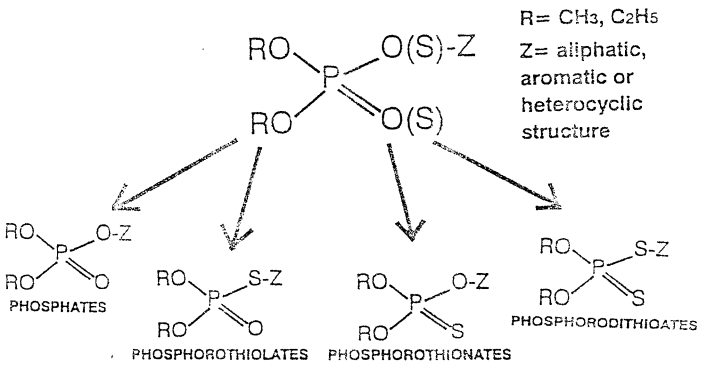
The types of marine areas at risk from contamination by organophosphorous discharges are river mouths and estuaries, lagoons, shallow waters and marshes.

The largest input of OP's in the marine environment comes through transportation of the compounds to the sea *via* surface waters. Industrial effluents containing OP residues may, however, also be discharged directly into shallow waters through pipelines from on-shore plants. Others sources of pollution may arise from spraying of crops with OP pesticides on fields nearby the sea. Finally, atmospheric transport from point or non-point sources also contributes to the pollution of coastal waters, lagoons and marshes.

Chemical structures and properties

OP compounds can be considered as derivatives of inorganic phosphorus compounds in which one or more hydrogen atoms have been replaced by organic groups. With a few exceptions (the RO group is substituted by NHiPr in some compounds, such as fenamiphos and isofenphos), the OPs can be described by the same general structural formula

In this formula R may be the methyl or the ethyl group and all combinations of oxygen and sulphur atoms attached to phosphorus as indicated are realized. The moiety Z exhibits a great diversity from aliphatic to aromatic and heterocyclic structures with additional substituents. The OPs can be classified into four main groups:



The diversity of physical properties of OP insecticides, due to the different structures and chemical composition (atoms of S, O, N, Cl, Br) (see annex 1), presents some challenges in developing a comprehensive multiresidue screen. The molecular weights of the pesticide compounds range from 141 to 466 and from 140 to 698 for the non-pesticides. The vapor pressures for the pesticides spans six order of magnitudes (from <0.001 to 1600 mPa (at 20 ^{0}C). For the non-pesticides the range spans four orders of magnitude: from less than 0.02 to 127 mm Hg. The water solubility of the pesticides also varies widely from one compound to another: from 0.14 mg/L for the least soluble, to 4 x 10^{6} mg/L for the most soluble. A large range is also found in the non-pesticides: from 0.36 mg/L to 7000 mg/L. The OP pesticides usually exhibit log K_{ow} values of between 3-4, although the range varies from 0.5 for trichlorfon to 5.95 for temephos (Bowman and Sans, 1983). For the non-pesticides, the lowest log K_{ow} value is for tris(2-chloroethyl)phosphate, and the highest, 6.08 for cumylphenyl diphenyl phosphate (Muir, 1984). OP pesticides in general, do not have a high bioaccumulation potential and, consequently they do not present a high hazard to biota from this point of view.

Toxicity

OP compounds are toxic because of their action on the nervous system. OP pesticides inhibit the enzyme acetylcholinesterase (AChE), leading to accumulation of toxic levels of endogenous acetylcholine in nervous tissue and effector organs which disturbs the correct functioning of the nervous system. Non-pesticide OP's are

disturbs the correct functioning of the nervous system. Non-pesticide OP's are dangerous compounds since they are known to induce a delayed neurotoxicity in warm-blooded vertebrates by interfering with another enzyme: the neuropathy target esterase (NTE), which hydrolyses phenylacetate or phenylvalerate. All OP pesticides are very toxic to aquatic biota. Insects and particularly crustaceans are extremely sensitive to intoxication by these pesticides, although they are wide differences between different species of the same group. Acute effects on marine crustaceans have been reported at concentrations of 1 µg/L for several OP pesticides (Schimmel *et al.*, 1983) and 150-200 µ/L for non-pesticide OP's. Chronic effects in the most sensitive aquatic biota have been found in the two groups at levels as low as 0.1 µg/L.

Degradation

The persistence of these compounds in the marine environment depend on the different degradation pathways including chemical, photochemical and biological processes. Hydrogen ion concentration, temperature, salinity, and microorganisms affect their persistence in the marine environment. These compounds are more stable in natural fresh and saline waters between pH 5 and 7 and less stable at pH's greater than 7 or less than 2. P=S containing organophosphorous compounds may be oxidized to their P=O oxon analogs by various chemical oxidants including bromine water, dinitrogen tetraoxide, N-bromosuccinamide, nitric acid, peracetic acid, hydrogen peroxide and potassium permanganate but not directly by molecular oxygen (In Brown et al, 1993). In generally, the half-live of these compounds in seawater range from few hours to few weeks (12 hours to 30 days) (Cotham and Bidleman, 1989; Lacorte and Barceló, 1994; Wang and Hoffman, 1991; Pritchard et al, 1987; Carvalho *et al.*, 1992), being the microbial activity the more rapidly degradation pathway. However, the faster degradation of these compounds in seawater compared to freshwater might result from the hydroxide-catalyzed hydrolysis which predominates in the marine environment. The hydrolysis rates of organophosphorous pesticides are dependent upon their chemical structure, pH and temperature. In pH 6.0 buffered solutions at 70 °C range from half lives of 0.5 h to 4.0 days. At 20 °C the rates are several hundred times slower (Rusicka, et al, 1967).

The relatively instability or short half-life of the OP is beneficial to the environment, but it also causes analytical problems. As many of these compounds can react to give

toxic metabolites by oxidation and isomerization before hydrolysis and detoxification occurs, the analyst is confronted with a problem of great complexity

Photodegradation studies in water using either sunlight or UV irradiation have shown a variety of photoalteration products, e.g. oxo derivatives and different phenols which may be even more toxic than the parent compounds.

1. SCOPE AND FIELD APPLICATION

The reference methods described in this manual are intended for use in seawater marine monitoring programmes to determine organophosphorous compounds. A standard methylene chloride liquid-liquid extraction (LLE) and an off-line liquid-solid phase extraction (SPE) procedures are provided. The first method can be successfully applied to most of the OP compounds whereas the second is restricted to the more hydrophobic compounds. However, the SPE technique has obvious advantages in minimizing solvent consumption, in minimizing the exposure of laboratory personnel to solvent vapors, and in being adaptable to field use. Other recent developments of immunoassays and enzyme-linked immunosorbent assays (ELISAs) for pesticide detection are not being considered in the present method.

Gas chromatography (GC) has undoubtedly been the most common technique for analysing these compounds because it can be combined with very sensitive detectors, such as nitrogen-phosphorus detector, flame photometric detector and atomic emission detector. Characterization by mass spectrometric analysis are also necessary for a reliable identification of the compounds on the chromatograms.

On the other hand, high-performance liquid chromatographic (HPLC) methods have grown in this application field due to possibility of determining thermally labile and polar compounds that are not GC amenable. LC detectors include UV scanning and diode array type detectors, electrochemical, MS and MS-MS. However, the use of HPLC is not really satisfactory because many OPs do not have a chromophoric group and, in general, UV absorption does not provide sufficient selectivity and/or sensitivity in environmental trace analysis. It should be taken into account that detection in LC-UV and LC-MS are usually at least 2.5 orders of magnitude lower than in GC-NPD and GC-MS (Durand *et al*, 1989). For this raison, to carry out the environmental

monitoring of organophosphorous pesticides at the low ng/L level, only the GC methods can be employed.

In these reference methods, only gas chromatographic methods using flame photometric, nitrogen/phosphorus thermionic and mass spectrometry detector are described to screen the compounds.

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3. GENERAL CONSIDERATIONS AND SAMPLE HANDLING

3.1. Sampling

A sample of 1 to 4 L is taken by means of a pre-cleaned solvent bottle, preferably from at least 10 cm below the surface in order to avoid sampling the surface film.

3.2. Sample pretreatment

LLE

The sample might be slightly acidified with concentrated acetic acid, reducing pH to 6.0.

SPE

Water samples containing a great amount of suspended particulate matter should be first prefiltered through glass filters (0.45 μm) before solid-phase extraction. In general, it will not affect the determination of the organophosphorus with log K_{oc} (partition coefficient between soil organic carbon and water) and log P_{ow} (n-octanol-water partition coefficient) around 2, since these compounds are largely distributed in the dissolved and not in the suspended phase of the water. However, for those compounds exhibiting a higher log K_{oc}, it will be necessary to distinguish between dissolved and particulate matter, and to look for the different types of pesticides in the filtrate and in the filter.

3.3. Sample handling and storage

LLE

Water to be transported back to the laboratory will be iced at 4°C until arrival at the laboratory, where it will be refrigerated at that temperature and extracted within 48 h of collection. These requirements are based on the high inestability of the organophosphorous compounds including in biologically inhibited water solutions stored at 4°C for 14 days (Munch and Frebis, 1992).

SPE

Solid-phase extraction can be successfully conducted in the field and offers several advantages over the traditional method of collecting and preserving water samples in glass bottles for laboratory extraction by LLE. Field-extracted samples require less space, and they are easily cooled and packaged for shipment to analytical laboratories. As these analytes show similar or greater stability in SPE disks compared to storage in water at 4°C, one of the most favorable storage options consist on freezing the solid-phase extraction columns or disks at -20 °C.

3.4. Cleaning of glassware

Scrub all non-volumetric glassware vigorously with brushes in hot water and detergent. Clean it in an ultrasonic bath containing a non-posphate detergent for 15 minutes. Rince with tap water, acetone and hexane. Bake overnight in an oven at 240 °C.

Volumetric glassware should be cleaned overnight in sulfo-chromic acid, rinced with tap water, acetone and hexane.

All clean glassware should be tightly sealed with precleaned aluminium foil and solvent-rinced before using it.

CAUTION: Care should be taken to avoid skin contact or inhalation of the sulpho-chromic acid.

4. EXTRACTION METHODS OF ORGANOPHOSPHORUS

In these methods, pesticide sample preparation is usually achieved by liquid-liquid extraction or by enrichment by solid-phase extraction.

4.1. Extraction by liquid-liquid extraction

4.1.1. Principle

Organophosphorous compounds exhibit a great variation in their physico-chemical properties and, consequently, their analyses requires the use of polar solvents in liquid-liquid extraction to recover the most polar compounds (monocrotophos, dimethoate, dichlorvos) from an aqueous phase. Dichloromethane is selected as it is one of the most polar solvents of those generally used for extraction of analytes from water and results in the recovery of a wider range of compounds. Among the OPs compounds that may be determined individually by this method are the following:

azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, EPN, ethion, fenitrothion, leptophos, malathion, methidathion, methylchlorpyrifos, methylparathion, monocrotophos, parathion, sulfotep, tetrachlorvinphos, tributylphosphate, triisobutylphosphate, tris(2ethylhexyl)phosphate, triphenylphosphate.

4.1.2. Reagents

1. Methylene chloride and ethyl acetate solvents (nanograde, redistill in glass if necessary).
2. Sulphate sodium
3. Sulphochromic mixture containing 4g potassium dichromate ($K_2Cr_2O_7$) in 1L of sulphuric acid.
4. Concentrated acetic acid
5 Sulphochromic mixture containing 4 g potassium dichromate ($K_2Cr_2O_7$) in 1 L of sulphuric acid.
6. Detergent
7. Individual stock solutions of standards containing 50 mg/100 mL of each OP pesticide are prepared in ethyl acetate and kept at 4°C in the dark. Calibration standards for the gas chromatographic analysis are also prepared, by appropriate dilution, in ethyl acetate at the concentration of 0.5 ng/µL. Chlorthion, who is used as internal standard, is prepared in acetone.

CAUTION: Because OPs are acetylcholinesterase inhibitors in mammals, extreme care must be exercised in their use. They should be handled with extreme care to avoid skin contact or inhalation.

4.1.3. Apparatus

1. Rotary evaporator, cooling water for condenser and heated water bath for sample (never set to exceed 30°C).
2. Supply of dry nitrogen.
3. Gas chromatograph (GC) equipped with capillary split/split-less or on-column injectors and an electronic data capture system. Either must have a nitrogen-phosphor detector or a flame photometric detector. Columns are described under section 5.
4. Muffle furnace for precombusting reagents.
5. Drying oven for glassware and reagents.
6. Glassware:

   2 L glass separating funnels.

A range of volumetric flasks, graduated measuring cylinders, pipettes and glass syringes.

7. Analytical balance.
8. Stainless tweezers, spatulas, aluminum foil.
9. Ultrasonic bath.

4.1.4. Method

Measure the water sample volume using a graduated cylinder of 1 L. Quantitatively transfer this proper aliquot of sample into a two-liter separatory funnel. Add chlorthion as internal standard (about 200 ng in acetone solvent) and shake the separatory funnel to homogenize the water. Add 30 mL of methylene chloride and shake the separatory funnel softly and carefully (to prevent losses of the solvent at the opening of the stopcock due to the pressure release). Repeat this carefully shaking several times until the pressure is reduced and then shake vigorously for 5 minutes.

Allow the solvent to separate from the sample, then draw the methylene chloride into a 250 mL flask. Perform a second and third extraction in the same manner. Additional 20 mL of ethyl acetate was added to the extract before being concentrated to about 10 mL in a rotaevapor at 30 ° C. This extract is dried over sulphate sodium and decanted in a calibrated test tube of 15 mL along with three rinses of ethyl acetate. The final volume was decreased to 50-500 µL by a stream of dry nitrogen before being analysed by gas chromatography.

4.1.5. Precision and accuracy

The recovery of individual organophosphorous compounds spiked into 1 L NaCl saturated (60g/L) bidistilled water with dichloromethane at a concentration of about 400-2400 ng/L was found to be higher than 60% (RSD< 27%; n=3) for the following selected organophosphorous compounds (Tolosa *et al.*, 1996): azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, EPN, ethion, fenitrothion, leptophos, malathion, methidathion, methylchlorpyrifos, methylparathion, monocrotophos, parathion, sulfotep, tetrachlorvinphos, TiBP, TBP, tris(2-ethylhexyl)phosphate, tributoxiethylphosphate.

4.2. Extraction by solid-phase extraction

4.2.1. Principle

Solid-phase extraction (SPE) is an alternative procedure that has been used extensively to remove nonpolar organic chemicals from water. In this procedure, the water sample is passed through a short bed of packing material (column or disk) which may contain functional groups of different polarity such as alkyl (C8 or C18)-bonded-silica phase, graphitized carbon black, or Amberlite XAD resins. The target compound is bound by the sorbent, and the extracted water is discarded. The analyte is then eluted from the column or disk and analyze by appropriate methods.

SPE is mostly used off-line, the sorbent being packed in disposable cartridges or disks. SPE disks have been proven to have more advantages than SPE cartridges for extraction of analytes from water. SPE disks contain smaller silica particles that are more densely packed and more uniform. These particles enmeshed in a Teflon matrix eliminate bed channeling of silica particles, which is expected to cause lower recoveries when extracting with SPE cartridges. Moreover, a higher flow rate can be achieved reducing considerably the time of extraction.

However, for polar pesticides in water, the extraction efficiency of C-18 phase and styrenedivinylbenzene (SDB) are lower than that of the LLE technique due to the low breakthrough volumes of these compounds when these materials are used. Consequently, other better trapping sorbents, such as Carbopack and Lichrolut cartridges appear to be much more effective for trapping polar pesticides than C-18 and SDB disks.

A typical sequence of SPE includes the following steps: activation of the sorbent (wetting with a suitable solvent), conditioning (replacing of the activation solvent by the aqueous phase), percolation of the water sample, clean-up (removal of interfering components), drying of the sorbent bed, elution of accumulated analytes and regeneration.

The method described below which uses 1 L of sample and octadecyl bonded silica or styrene divinylbenzene disks show only good recoveries for compounds with water solubilities below 300 mg/L or with log K_{ow} greater than 2. Thus, poor recoveries are obtained for dichlorvos, monocrotophos and dimethoate (Tolosa *et al.*, 1996).

4.2.2. Reagents

1. Methanol and ethyl acetate solvents.

2. Sulphate sodium.

3. Filters, glass fiber GF/C, 47 mm (in the case of great amount of particles in the sample).

4. Empore extraction disks of 4.7 cm containing Bakerbond C_{18} or SDB copolymer: J.T. Baker

5. Sulphochromic mixture containing 4 g potassium dichromate ($K_2Cr_2O_7$) in 1 L of sulphuric acid.

6. Detergent

7. Individual stock solutions of standards are prepared in ethyl acetate and kept at 4°C in the dark. Calibration standards for the gas chromatographic analysis are also prepared in ethyl acetate. Chlorthion, who is used as internal standard, is prepared in acetone.

CAUTION: Because OPs are acetylcholinesterase inhibitors in mammals, extreme care must be exercised in their use. They should be handled with extreme care to avoid skin contact or inhalation.

4.2.3. Apparatus and equipment

1. Vacuum pump.

2. Rotary evaporator, cooling water for condenser and heated water bath for sample (never set to exceed 30°C)

3. Muffle furnace for precombusting reagents

4. Drying oven for glassware and reagents.

5. Gas chromatograph (GC) equipped with capillary split/split-less or on-column injectors and an electronic integrator o acquisition data. Either must have a nitrogen-phosphor detector or a flame photometric detector. Columns are described under section 5.

4. Glassware:

Assembly for 47 mm filters, with 300 mL funnel top, fritted glass funnel support, aluminum clamp and silicone rubber. (Standard Millipore 47-mm filtration glassware)

1000 mL side arm flask for vacuum filtration.

100 mL side arm flask for vacuum filtration.

A range of volumetric flasks, graduated measuring cylinders, pipettes and glass syringes.

5. Vacuum tube in latex.
6. Stainless tweezers, spatulas, aluminum foil.
7. Ultrasonic bath.
8. Supply of dry nitrogen.

4.2.4. Method

Octadecyl-silica or polystyrenedivinylbenzene co-polymer disks are first activated by wetting with 5 mL methanol and are then washed with 3 x 10 mL ethyl acetate to remove any contaminants from the disk. Subsequently, the disk is vacuum dried for 3 min. Methanol (15 mL), and bidistilled water (20 mL) are then pulled through the disks prior to use. The sample (1 L) spiked with chlorthion (200 ng in acetone) as the internal standard is extracted at a rate of 30 mL/min. The disk is dried briefly under vacuum, and compounds are eluted with 3 x 10 mL ethyl acetate for the 4.7 cm diameter membrane. During each application of ethyl acetate, the vacuum was applied and removed quickly to allow some ethyl acetate to penetrate the entire thickness of the disk. The vacuum is then reapplied, and the remainder of the ethyl acetate is eluted into a vacuum flask of 125 mL. Finally, the ethyl acetate is dried over anhydrous sodium sulfate and decanted into a flask of 100 mL along with three rinses of ethyl acetate. This extract is concentrated to a 6-10 mL in a rotatory evaporator, decanted in a calibrated test tube of 15 mL along with three rinses of ethyl acetate. The final volume was decreased to 50-500 µL by a stream of dry nitrogen before being analysed by gas chromatography.

4.2.5. Precision and accuracy

The recovery of individual organophosphorous compounds spiked into 1 L bidistilled water at a concentration of about 400-2400 ng/L was found to be higher than 75% (RSD< 18%; n=3) for the following selected organophosphorous compounds (Tolosa *et al.*, 1996): azinphos-ethyl, azinphos-methyl, chlorpyrifos,

chlorthion, coumaphos, diazinon, EPN, ethion, fenitrothion, leptophos, malathion, methidathion, methylchlorpyrifos, methylparathion, parathion, sulfotep, tetrachlorvinphos, TiBP, TBP, tris(2-ethylhexyl)phosphate, tributoxiethylphosphate.

5. GAS CHROMATOGRAPHIC DETERMINATIONS

The identification of the organophosphorous compounds by selective gas chromatographic separation may be corroborated through the use of two or more capillary columns of different polarity. The so-called primary column, generally a DB-1701 (14% cyanopropyl-phenyl-methylpolysiloxane), and a second column, called a confirmatory column, such a DB-5 (5% diphenyl and 95% dimethyl polysiloxane) are recommended to be used. However, some polar OP insecticides, such as acephate and methamidophos, do not chromatograph well on the nonpolar DB-5.

Multiresidue GC analysis is generally performed by hot splitless injection because of the ease of exchanging the injector inlet when it becomes contaminated with non-volatile deposits from the matrix. However, this injection technique is less precise and suitable for thermolabile OPs than cold on-column injection (Stan and Goebel, 1984).

In the splitlless mode, full efficiency of the column is realized by reconcentration of the sample components in a narrow band on the column prior to analysis, either by using a solvent effect or the effect of condensation of the solutes at the column inlet. The latter mechanism operates effectively for compounds with boiling points about 150 °C above the column temperature. Compounds with lower boiling points need a solvent effect for reconcentration. The solvent effect focuses the analytes on the head of the column. The oven temperature should be set to 10-30 °C below the boiling point of the solvent. The column temperature can then be raised to the temperature required. The temperature of injector should allow a rapid evaporation of solvent and solutes but it should be low enough to avoid destruction of sensitive components. The splitless mode allows a relatively large amount (0.5-3 µl) of dilute sample to be injected into a simple open glass tube liner in the injector port. The volume of this insert liner must accommodated quantitatively the vapour volume of the sample to avoid loss of analytes and memory peaks. It should also be periodically cleaned in chromic acid mixture overnight, followed by rincing with water, acetone, hexane and desactivation

by sililization. Aliquots of 1-2 µl might be injected in the splitless mode using a "hot needle technique".

The on-column technique allows the injection of a liquid sample directly into the inlet of the column, and this eliminates the possibility of sample loss during vaporization and transfer from the vaporizer to the column. The needle of the syringe must reach far enough into the column to avoid the sample components being transferred back into the injector block. To avoid a fast deterioration of the column a deactivated retention gap is recommended to couple in front of the analytical column via a press fit connector.

Detection and measurement are best accomplished by flame photometric gas chromatography using a phosphorus specific filter. The nitrogen-phosphorus detector, may also be used but with less specificity, and electron capture detector for those compounds to which it responds. Confirmation of the identity of the compounds should be made by GC-MS in the electron impact mode or negative chemical ionisation for those compounds to which it responds. Confirmation with a detector other than mass spectrometry requires the use of a second column that exhibits a different retention time for all analytes.

5.1. Detection with flame photometric detector (GC-FPD)

The FPD is a highly sensitive and selective detector for sulfur and phosphorus compounds. When a sulfur or phosphorus containing compound is combusted in a hydrogen-rich flame, chemiluminescent species such as S_2 or HPO are produced. By monitoring the characteristic emission of these species (394 nm for sulfur and 526 nm for phosphorus), detection and quantification of sulfur or phosphorus containing pesticides can be made. The FPD detects sulfur or phosphorus compounds by burning the column effluent in a tuned flame and measuring a selected spectral portion of the emission above the flame. Light emission at a wavelength characteristic of the phosphorus species passes through the 526 nm optical filter to a photomultiplier tube where it is converted to a current and amplified.

As the dynamic range of FPD is rarely more than two decades, the linearity of the FPD must be checked for each analyte. The detection limit of this detector with the phosphorous filter is about 10-100 pg.

Carrier gas can be hydrogen, helium or nitrogen depending on the availability of high quality grades. Hydrogen carrier, generally show the better chromatographic resolution but safety cut offs must be included when it is used.

Table 1 exemplifies the chromatographic conditions that may be applied to analyse the OP compounds by GC-FPD. Figure 1 illustrates the example of chromatogram for selected OPs using these conditions.

Table 1. Conditions for a capillary GC-FPD.

Carrier gas: helium at a flow-rate of 1.5 mL/min

Column: 25 m x 0.25 mm I.D. x 0.20 μm Chrompack OV-1701.

Injector temperature: Splitless: 250 °C

Detector temperature: 225 °C.

Temperature programme: 60 °C for 1 min; 60 °C to 190 at 25 °C/min, 190 °C to 225 °C at 2 °C/min, 225 °C to 280 °C at 5 °C/ min, 280 °C isothermal for 10 min;

5.2. Detection with nitrogen-phosphour detector (GC-NPD).

The nitrogen-phosphorus detector (NPD) uses a jet and collector similar to the universally employed FID. However, the collector contains a small alumina cylinder coated with a rubidium salt (the active element) and heated electrically. In the presence of this thermonionic source, nitrogen and phosphorus containing organic molecules are efficiently ionized. Ions are collected and the resulting current measured.

Hydrogen and air are required, but at flows significantly less than normal FID operation. Thus, the flame is not actually ignited but it glows on the surface of the heated alkali source (rubidium salt) to produce dissociation of ions. The advantage of this arrangement is that normal hydrocarbon ionization reactions associated with the FID do not proceed efficiently and thus the detector provides high selectivity towards nitrogen and phosphorus containing compounds. However, accurate control of the

hydrogen flow rate is important due to the fact that the NPD response depends on the concentration of the H atoms in the gaseous boundary layer of the bead.

As, the NPD is a destructive and mass flow-rate dependent detector, "the constant-flow" mode should preferably be used or coinjection of internal standards is recommended to increase quantitative accuracy.

Care should be taken to turn off the collector voltage while the detector gases are interrupted (i.e. during changing of the septum, column, gas cylinders, etc.). Gas supplies must be free of moisture to avoid a fast deterioration of the active element.

The selection of the carrier gas is also important. When helium is used, the NPD response may decrease to only 10% of that measured using nitrogen because of increased cooling of the alkali source and incomplete decomposition of the sample.

The NPD offers a dynamic range of 2 to 3 decades and the detection limit for OPs is about 30 to 200 pg.

Figure 2 and 3 illustrates two chromatograms obtained by GC-NPD with different conditions and different columns.

5.3 Quantification

The chromatograph is first calibrated by injecting an appropriate standard mixture which includes the surrogate standard (chlorthion) used in the analysis. Prior to use as a quantitative instrument, the linear range of response must be determined by injecting a series of standard mixtures of OPs and constructing calibration curves. Quantitative analysis can only be conducted when the concentrations of analytes are within the linearly calibrated range. Response factors (RFs) are calculated in terms of area. ng^{-1}

Organophosphorus in samples are determined by injecting a known aliquot of the organic extracts into the GC. Peak areas are integrated and amounts calculated from the RFs of the external standards. Recoveries of the surrogate standard should also be evaluated for losses through the analytical procedure. These values should be better than 70% recovery, otherwise the analytical procedure must be checked.

The external standard method uses absolute response factors, the internal standard method is calibrated in terms of response ratios. In external standard methods, the sample amount injected must be highly reproducible. The method is well suited to

automatic mechanical methods of injection. On the other hand, the internal standard method is independent of sample size and compensates for any slight instrumental drift. When used properly, it is the most accurate method of calculation.

The calculations are exemplified below:

External standard method

Compute RFs from external standard run as area. ng^{-1}.

Compute XF (dilution factor) as total extract volume (μL) divided by μL injected.

$$\text{Recovery chlorthion (REC)} = \text{Peak area on GC} \times \frac{1}{\text{RF of chlorhion}} \times \text{XF} \times \frac{1}{\text{ng chlorhion added to sample}}$$

$$\text{[paration] (ng / L)} = \text{Peak area on GC} \times \frac{1}{\text{RF of parathion}} \times \text{XF} \times \frac{1}{\text{REC chlorthion}} \times \frac{1}{\text{L sample}},$$

Internal standard method:

$$\text{[paration] (ng / L)} = \frac{\text{Peak area parathion}}{\text{Peak area chlorthion}} \times \frac{\text{RF chlorthion}}{\text{RF parathion}} \times \frac{\text{total ng chlorthion added to sample}}{\text{L sample}}$$

5.4. Confirmation by mass spectrometry

In order to avoid "false positives" in the determination of pesticides in water samples, GC-MS, in electron impact (EI) mode by the selective ion monitoring or the full scan mode, is the most widely used confirmation technique. GC/MS on negative or positive chemical ionization can be also successfully applied to those compounds to which it responds.

Peak confirmation is achieved by evaluating the retention time of the peaks on the chromatograms and evaluation of the associated spectrum. In the case of quantification by GC/MS/EI, the spectra are also used to determine if any coeluting substances are contributing to the areas of target ions to be used for the quantification.

The practical detection limit for GC/MS/EI analysis in scan mode is generally in the range of 5 to 10 ng per compound injected. Sensitivity is greatly increased by acquiring the data in the selected ion monitoring or SIM mode. In this procedure, the time windows for ion monitoring are established with scan data for pure compounds. For routine EI-SIM acquisition, Table 2 lists some confirmatory ions and the approximate percent relative abundances, which can be be used as a first level of confirmation of peak identity for SIM data. However, as these percentages can vary significantly from

one instrument to another, depending on the calibration tune and conditions, it is recommended to calibrate your mass spectrometer with real standards to confectioner your own percent relative abundances. The detection limit for OPs in electron impact and SIM mode is generally in the range of 50 pg per compound injected.

For the OPs compounds exhibiting a high electronic affinity, the mass spectrometry in the chemical ionization (CI) mode may facilitate the identification of these compounds at trace levels due to the high selectivity of this technique. Interferences are found to be less dominant than in EI mode, specially in the negative mode (NICI). Sensitivity for the determination of OPs is in general much better in NICI than in positive mode (PICI) or in EI ionization, depending on the electron affinity of the compound. Table 2 lists some confirmatory ions and the approximate percent relative abundances in the NICI technique using methane as a reagent gas. Caution should be taken with these abundances because they are dependent on the instrumental parameters, pressure and temperature of the ion source, concentration of the compound, presence of oxygen and instrument type.

Table 2. Target compounds analysis by gas chromatography-mass spectrometry in the electron impact (EI) and negative ion chemical ionization (NICI) scanning from m/z 100 to 500. (From Busch *et al.*, 1978; Stan and Kellner, 1982; Liao *et al.*, 1991; Lacorte *et al.*, 1993; Hites, 1992; Agüera *et al.*, 1993)

Compound name	M.W.	EI	NICI
		m/z, % relative abund.	m/z, % relative abu
Acephate	183	136(100), 125(12), 183(7)	
Amidithion	273		157(100)
Azinphos-ethyl	345	132(100), 160(82), 104(19)	185(100), 133(4)
Azinphos-methyl	317	160(100), 132(84), 104(30)	157(100), 133(12)
Bromophos	364	331(100), 329(80), 125(65)	257(100), 141(66), 27
Bromophos-ethyl	392	303, 359	257(100), 358(59), 33
Carbophenothion	342	157(100), 121(48), 342(30)	185(100), 143(52)
Chlorfenvinphos	358	267(100), 323(76), 269(63)	153(100)
Chlorpyrifos	349	197(100), 199(92), 314(54)	313(100), 212(61), 16
Chlorphyriphos methyl	321	125(100), 109(25), 286(60)	
Chlorthion	297	109(100), 125(97), 297(40)	188(100), 297(20), 15
Coroxon	346	109(100), 346(91), 210(80)	
Coumaphos	362	362(100), 109(95), 226(78)	225(100), 362(28), 16
Coumithoate	368	216(100), 368(90), 125(76)	
Cyanofenphos	303	157(100), 149(55), 169(55)	
Cyanophos	243	109(100), 125(45), 243(40)	
Cythioate	297	125(100), 109(94), 297(40)	
Demeton-O	258	115(100),171(90), 143(70)	169(100), 229(8), 95(
Demeton-S	258	114(100), 170(80), 143(65)	169(100), 229(8), 95(
Demeton-S-methyl	230	109(100), 142(70)	141(100), 215(64), 9
Demeton-S-methylsulfon	262		141(100), 247(13)
Dialifor	393	208(100), 210(42), 347(10)	185(100), 173(51)
Diazinon	304	137(100), 179(75), 152(65)	169(100)
Dicapthon	300	262(100), 125(64), 216(20)	
Dichlofenthion	314	279(100), 223(50), 281(42)	285(100), 278(81), 2
Dichlorvos	220	109(100), 185(25), 145(7)	125(100), 134(28), 2
Dicrotophos	237	127(100), 193(15)	125(100), 224(14)
Dimethoate	229	125(100), 143(20), 229(10)	157(100)

Compound name	M.W.	EI	NICI
		m/z, % relative abund.	m/z, % relative abund.
Dioxathion	456	125(100), 153(30), 270(30)	153(100), 185(<1)
Disulfoton	274	142(100), 186(70), 274(75)	185(100)
EPN	323	157(100), 169(65), 185(38)	138(100), 323(38)
Ethion	384	231(100), 153(85), 125(80)	185(100)
Ethoprop	242	158(100), 139(58), 126(40)	199(100)
Etrimfos	292	125(100), 109(43), 292(36)	
Famphur	325	218(100), 125(61)	
Fenamiphos	303	154(100), 303(87), 217(54)	153(100)
Fenchlorphos	320	285(100), 125(65), 109(28)	211(100), 141(37), 270(13)
Fenitrooxon	261		261(100)
Fenitrothion	277	109(100), 125(97), 277(67)	168(100), 277(84), 141(29)
Fensulfothion	308	125(100), 141(85), 293(80)	169(100), 293(19), 171(14)
Fenthion	278	278(100), 125(70), 169(30)	263(100), 141(52), 277(10)
Fonofos	246	109(100), 137(60), 246(46)	169(100), 109(72)
Formothion	257	125(100), 126(70), 170(20)	157(100)
Heptenophos	251	124(100), 109(40), 250(7)	
Iodofenphos	412	377(100), 125(44), 379(37)	
Iprobenfos	288	204(100), 288(18), 246(18)	
Lepthophos	410	171(100), 377(62), 375(45)	241(100), 239(61), 243(46)
Malaoxon	314	127(100), 109(30), 195(15)	141(100), 172(9)
Malathion	330	127(100), 125(100), 173(95)	157(100)
Mecarbam	329	131(100), 125(49), 329(12)	
Menazon	281	156(100), 125(24), 281(19)	
Methamidophos	141	141(100), 111(19)	
Methidathion	302	145(100), 125(20)	157(100)
Mevinphos-beta	224	127(100), 192(24), 109(32)	125(100)
Mevinphos-alpha	224	127(100), 192(30), 109(25)	
Monocrotophos	223	127(100), 109(22), 192(7)	125(100), 208(9)
Naled	378	109(100), 145(53)	251(100), 205(43), 160(33)
Omethoate	213	110 (100), 125 (17), 213(4)	141(100), 198(7)
Parathion	291	109(100), 139(40), 291(35)	154(100), 291(28), 169(14)

Compound name	M.W.	EI	NICI
		m/z, % relative abund.	m/z, % relative abund.
Parathion-methyl	263	263(100), 149(64), 109(99)	154(100), 263(67), 141(22)
Paraoxon	275	109(100), 220(20), 275(20)	275(100), 153(40), 152(25)
Paraoxon-methyl	247		247(100)
Phenkapton	376		177(100), 185(89)
Piperophos	353	122(100), 140(80), 320(50)	
Pirimiphos-ethyl	333	333(100), 318(82), 304(58)	
Pirimiphos-methyl	305	290(100), 276(90), 305(65)	
Phorate-O		171(100), 111(75), 143(45)	
Phorate	260	121(100), 260(38), 231(29)	185(100)
Phosalone	367	182(100), 184(35), 121(65)	185(100)
Phosmet	317	160(100), 161(15), 317(2)	157(100), 207(14), 161(9)
Phosphamidon	299	127(100), 264(46), 138(35)	125(100), 178(46), 249(41)
Phoxim	298	129(100), 157(78), 298(15)	169(100)
Profenofos	374	139(100), 208(75), 339(30)	
Prothoate	285	115(100), 285(8), 121(18)	
Pyrazophos	373	221(100), 232(31), 373(22)	373(100), 169(40), 236(9)
Pyridafenthion	340	199(100), 188(89), 340(79)	340(100), 169(40)
Quinalphos	298	146(100), 298(170)	
Ronnel	320	125(100), 285(97), 287(64)	211(100), 213(99), 141(20)
RPA-400629	368	171(100), 121(31), 215(30),	185(100), 169(49)
Stirofos	366	109(100), 331(66),	125(100)
Sulfotepp	322	322(100), 202(53), 266(39)	293(100), 169(38), 277(12),
Temephos	466	466(100), 125(51), 203(10)	
Terbufos	288	103(100), 231(59), 153(45)	
Tetrachlorvinphos	364	109(100), 329(84), 331(80)	125(100)
Thiomethon	246	125(100), 158(10)	
Thionazin	248	107(100), 106(73), 143(52)	
Triamiphos	294		293(100)
Triazophos	313	161(100), 162(80), 257(30)	95(100), 312(31), 169(29)
Trichlorfon	256	109(100), 110(75), 139(60)	147(100), 170(19), 134(14)
Vamidothion	287	145(100), 142(53), 109(53)	141(100), 272(10), 259(10)

6. QUALITY ASSURANCE

Guidelines for data acquisition and data quality evaluation in environmental chemistry are published by UNEP (Reference Method 57) and by the American Chemical Society (ASC, 1980).

It has been recommended that a reference material should be analysed periodically to check on the quality of analytical data. Nowadays, there is no a reference material for OPs compounds in waters, and consequently, the accuracy of the method can not be checked. However, analysts should use their own specially prepared reference material for quality control purposes to check the precision of their measurements.

One approach consist on the *recovery test method*, which can be determined by analysing samples to which have been added known amounts of analyte. This procedure has the limitation that the added analyte is not necessarily in the same form as that naturally present in the sample matrix and, because of its more availability , may give unduly optimistic recovery figures.

Recovery test method

Make a recovery test by spiking three subsamples of a seawater sample with appropriate amount of pesticides (between 100 and 500 ng/L depending on the expected concentration). Analyse the unspiked and spiked subsamples in the same way as is described for the samples. Calculate the recoveries according to the 5.3 section. For those analytes naturally present in the unspiked sample, corrected recoveries of the analytes should be calculated by subtracting the amount of analyte naturally present in the unspiked seawater sample.

7. SOURCES OF REAGENTS AND APPARATUS.

Organophosphorus (OPs) standards: Riedel-de Haën (Seelze, Germany)

Standard Millipore (47-mm) filtration glassware

Empore extraction disks of 4.6 cm containing Bakerbond C_{18} and SDB copolymer: J.T. Baker

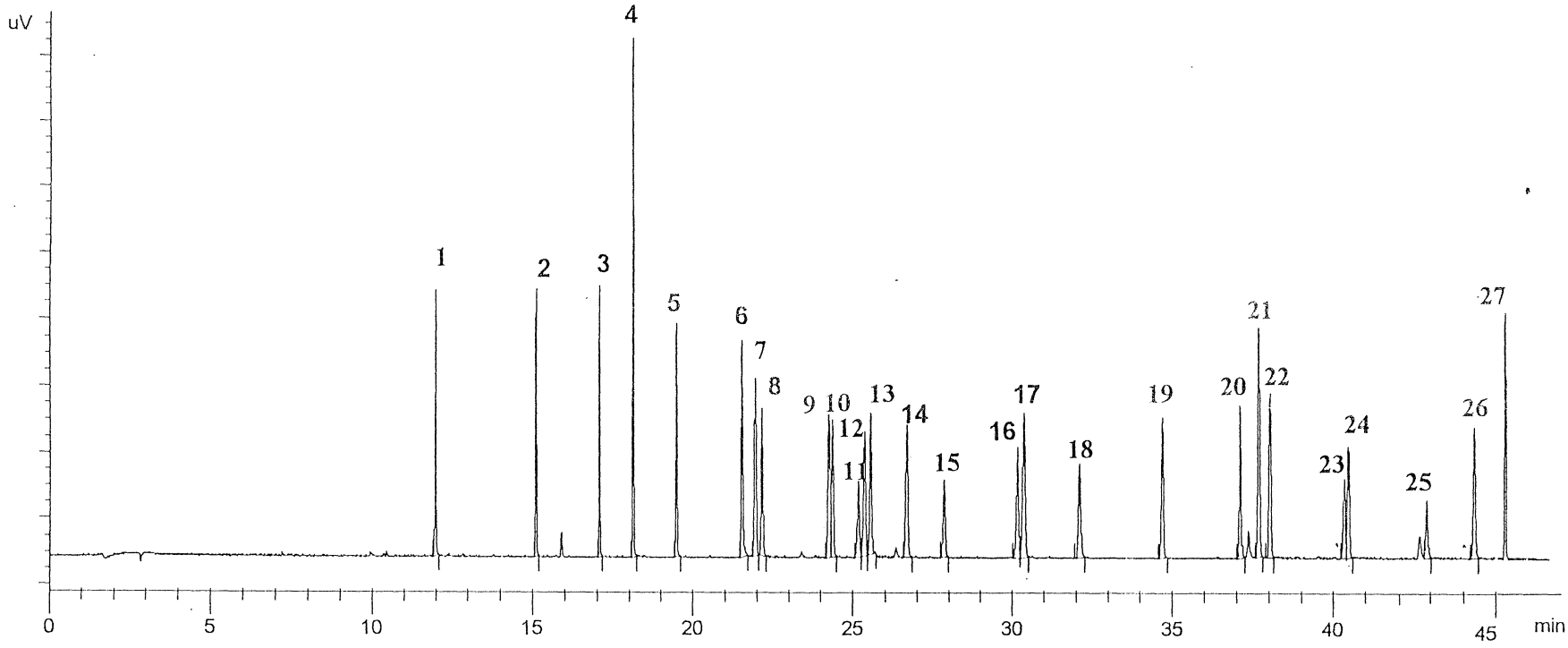


Fig. 1. GC-FPD chromatogram for organophosphorous standards. Peaks: 1= Dichlorvos; 2= TiBP; 3= TBP; 4= Sulfotep; 5= Diazinon; 6 = Monocrotophos; 7= Methylchlorpyrifos; 8= Dimethoate; 9= Chlorpyrifos; 10= Parathion-methyl; 11= Fenthion; 12= Malathion; 13 = Fenitrothion; 14= Parathion-ethyl; 15= Chlorthion; 16= Tetrachlorvinphos; 17= Methidathion; 18= Fenamiphos; 19= Ethion; 20= Tris(2ethylhexyl)phosphate; 21= Triphenylphosphate; 22= Tributoxiethylphosphate; 23= Leptophos; 24= EPN; 25= Azinphos-methyl; 26= Azinphos-ethyl; 27= Coumaphos.

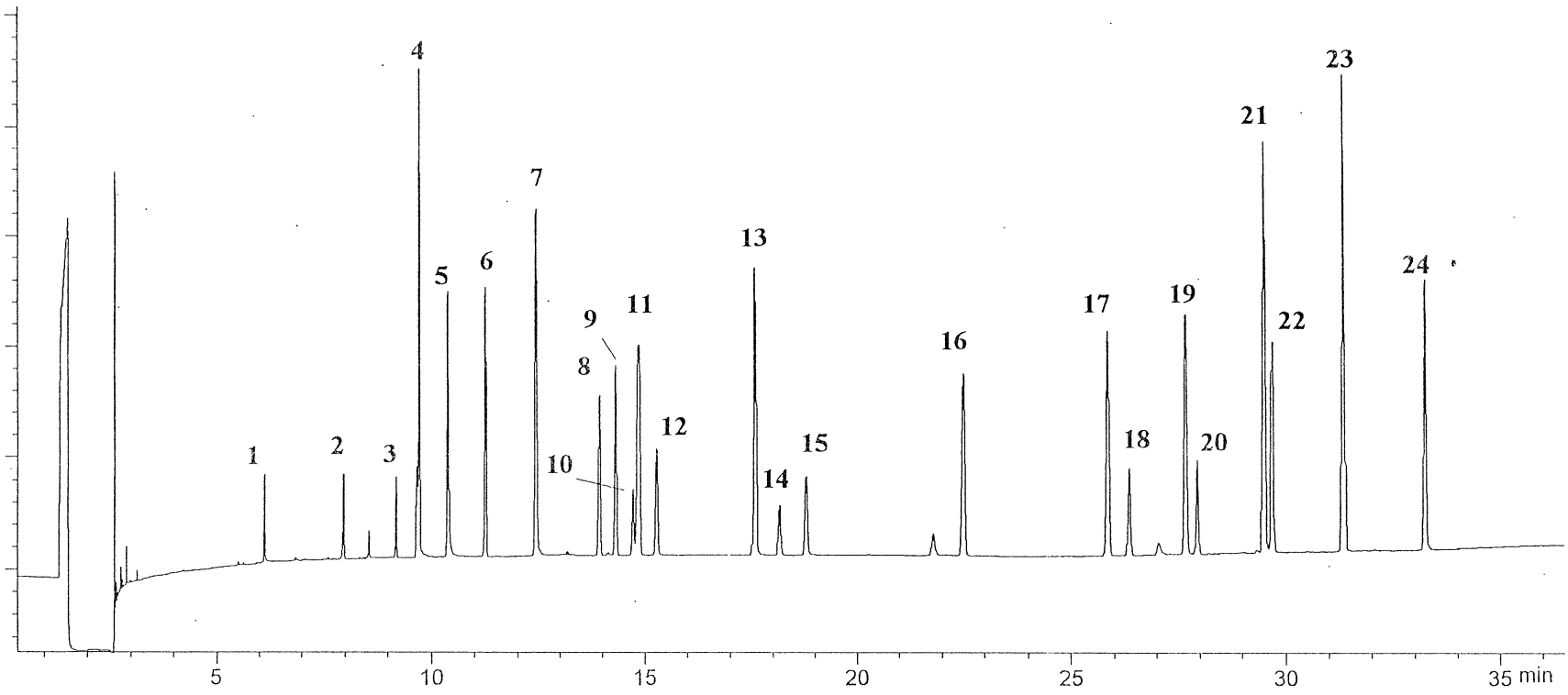


Fig. 2. GC-NPD chromatogram for organophosphorous standards. Peaks: 1= Dichlorvos; 2= TiBP; 3= TBP; 4= Monocrotophos and Sulfotep; 5= Dimethoate; 6= Diazinon; 7= Methylchlorpyrifos and Parathion-methyl; 8= Fenitrothion; 9= Malathion; 10= Fenthion; 11= Chlorpyrifos and Parathion-ethyl; 12= Chlorthion; 13= Methidathion;14= Tetrachlorvinphos; 15= Fenamiphos; 16= Ethion; 17= Triphenylphosphate; 18= Tributoxiethylphosphate; 19= EPN; 20= Tris(2ethylhexyl)phosphate; 21= Azinphos-methyl; 22= Leptophos; 23= Azinphos-ethyl; 24= Coumaphos.

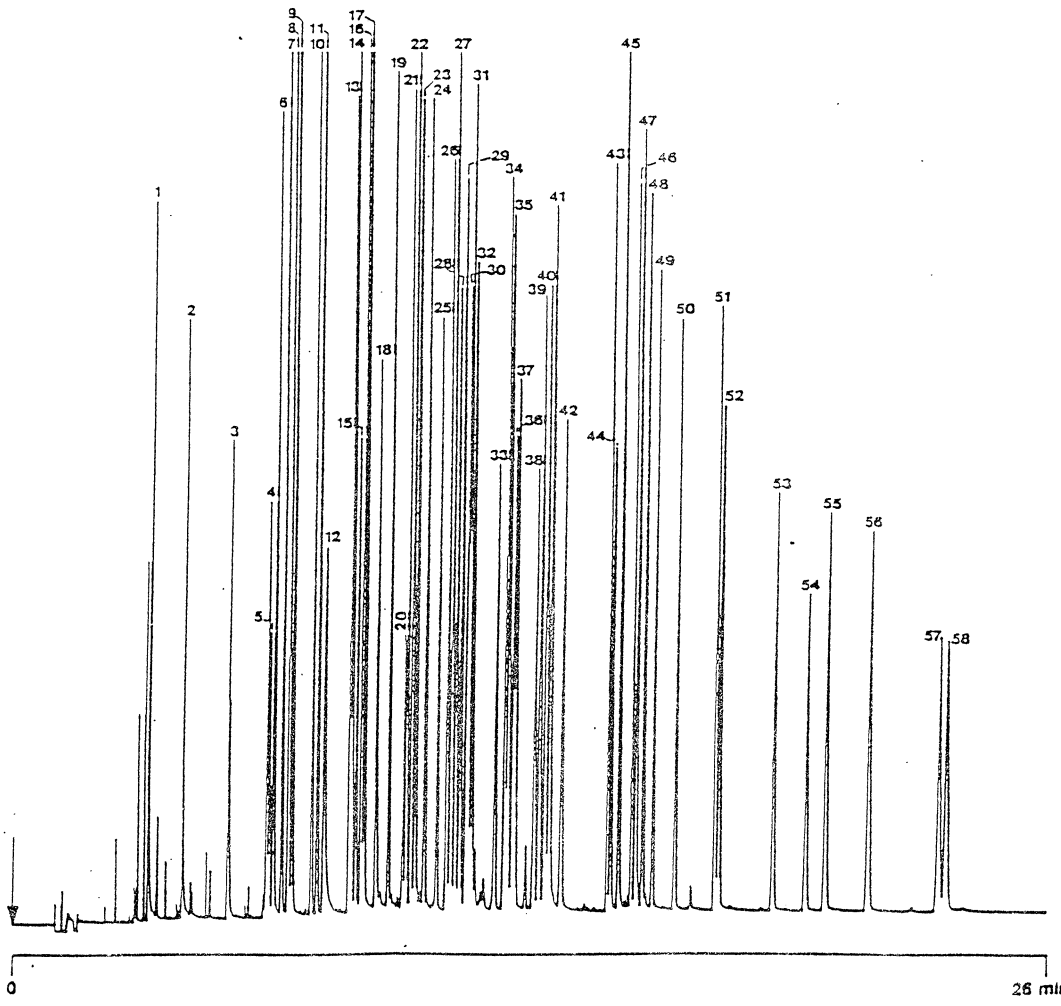
Conditions:30 m x 0.25 mm i.d.x 0.25 μm PTE-5 (5% phenylmethylsilixone). Injector temperature: Splitless: 250 ^{o}C; Detector temperature: 225 ^{o}C; Temperature programme: 60 ^{o}C for 1 min; 60 ^{o}C to 190 at 25 ^{o}C/min, 190 ^{o}C to 225 ^{o}C at 2 ^{o}C/min, 225 ^{o}C to 280 ^{o}C at 5 ^{o}C/ min, 280 ^{o}C isothermal for 10 min.

Fig. 3.

Separation of organophosphorous pesticides

Chr

Column	:	CP-Sil 13 CB fused silica WCOT 50 m x 0.32 mm; df = 0.4 µm Cat.no. 7937
Temperature	:	80°C - 270°C, 20°C/min
Carrier gas	:	H_2, 100 kPa (1.0 bar, 14 psi)
Injector	:	on-column
Detector	:	NPD
Sample size	:	1 µl
Concentration range	:	1 ng/compound
Courtesy	:	Mr. Lembacher, Hipp K.G., Pfaffenhofen Germany



Peak identificatio

1. triethyl phosp
2. dichlorvos
3. mevinphos
4. tinox
5. TCPP
6. heptenophos
7. tributyl phosp
8. phorate oxon
9. ethoprophos
10. sulfotep
11. phorate
12. monocrotoph
13. dimethoate
14. diazinon
15. dioxathion
16. cyanophos
17. disulfoton
18. paraoxon-met
19. dichlophethiol
20. malaoxon
21. dursbanmethy
22. methyl parathi
23. ronnel
24. pirimiphos met
25. malathion
26. dursbanethyl
27. ethyl parathion
28. trichloronate
29. pirimiphosethy
30. cruforuate
31. chlorthion
32. bromophos-me
33. chlorfervinphos
34. quinalphos
35. phenthoate
36. bromophos eth
37. prophaphos
38. tetrachlorvinph
39. methidathion
40. fenaminphos
41. bromfenvinpho
42. profenphos
43. ethion
44. fensulfothion
45. triaminphos
46. triazophos
47. carbophenothio
48. famphur
49. edifenphos
50. triphenyl phosp
51. EPN
52. phenkapton
53. phosalon
54. azinphos methy
55. pyrazophos
56. azinphos ethyl
57. coumaphos
58. tri-p-cresyl phos

Annex 1. List of the organophosphorous pesticides most used worldwide (Royal Society of Chemistry, 1987; British Crop Protection Council, 1983)

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Acephate	*O,S*-dimethyl acetylphosphoramidothioate	183.2	790000	0.226 (24)	
Amidithion	*S*-2-methoxyethylcarbamoylmethyl *O,O*-dimethyl phosphorodithioate	273			
Anilofos	*S*-4-chloro-*N*-isopropylcarbaniloylmethyl *O,O*-dimethylphosphorodithioate	367.5	13.6	2.2 (60)	
Azamethiphos	*S*-6-chloro-2,3-dihydro-2-oxo-oxazolo[4,5-b]pyridin-3-ylmethyl *O,O*-dimethyl phosphorothioate	324.7	1100	0.005 (20)	
Azinphos-ethyl	*S*-3,4-dihydro-4-oxobenzo[d]-[1,2,3]-triazin-3-ylmethyl) *O,O*-diethyl phosphorodithioate	345.4	4-5	<0.029 (20)	3.4
Azinphos-methyl	*S*-(3,4-dihydro-4-oxobenzo[d]-[1,2,3]-triazin-3-ylmethyl) *O,O*-dimethyl phosphorodithioate	317.1	29 (25)	<0.001 (20)	2.7
Bensulide	*O,O*-diisopropyl S-2-phenylsulphonylaminoethyl phosphorodithioate	397.5	25	<0.133 (25)	
Bialaphos	L-2-amino-4-[(hydroxy)(methyl)phosphinoyl]butyryl-L-alanyl-L-alanine	323.3	1000000		
Bromophos	*O*-4-bromo-2,5,-dichlorophenyl *O,O*-dimethylphosphorothioate	366.0	0.7	17 (20)	4.9

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Crotoxyphos	dimethyl (*E*)-1-methyl-2-(1-phenylethoxycarbonyl)vinyl phosphate	314.3	1000	1.9 (20)	
Cyanofenphos	*O*-4-cyanophenyl-*O*-ethyl phenylphosphonothioate	303.3	0.6 (30)	0.001 (20)	
Cyanophos	*O*-4-cyanophenyl *O,O*-dimethyl phosphorothioate	243.2	46 (30)	105 (20)	2.74
Demeton-O	*O,O*-diethyl *O*-[2-(ethylthio)ethyl]phosphorothioate	258.3	60	34 (20)	
Demeton-S	*O,O*-diethyl *S*-[2-(ethylthio)ethyl]phosphorothioate	258.3	2000	34(20)	
Demeton-S-methyl	*S*-2-ethylthioethyl *O,O*-dimethyl phosphorothioate	230.3	3300	48 (20)	
Demeton-S-methylsulphone	*S*-2-ethylsulphonylethyl *O,O*-dimethyl phosphorothioate	262.3	3300	0.66 (20)	
Dialifos, Dialifor	*S*-2-chloro-1-phthalimidoethyl *O,O*-diethyl phosphorodithioate	393.8	< 1	133 (35)	
Diazinon	*O,O*-diethyl *O*-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate	304.3	40	0.097 (20)	3.8
S,S-di-sec-butyl O-ethyl phosphorodithioate	*S,S*-di-sec-butyl *O*-ethyl phosphorodithioate	270.4	248	120 (25)	
Dicapthon	O-2-chloro-4-nitrophenyl O,O-dimethyl phosphorothioate	300			3.6
Dichlofenthion	*O*-(2,4-dichlorophenyl) *O,O*-diethyl phosphorothioate	315.2	245		5.38
Dichlorvos	2,2-dichlorovinyl dimethyl phosphate	221.0	10000	1600 (20)	1.5
Dicrotophos	(*E*)-2-dimethylcarbamoyl-1-methylvinyl dimethyl phosphate	237.2	Misc.	9.3 (20)	
Dimethoate	*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate	229.2	25000	1.1 (25)	0.8

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Bromophos-ethyl	*O*-4-bromo-2,5-dichlorophenyl *O,O*-diethylphosphorothioate	394.0	0.14	6.1 (30)	5.7
Butamifos	*O*-ethyl *O*-6-nitro-*m*-tolyl *sec*-butylphosphoramidothioate	332.4	5	84 (27)	
Carbophenothion	*S*-(4-chlorophenylthio)methyl *O,O*-diethylphosphorodithioate	342.9	< 1	1.07 (25)	5.1
Chlorfenvinfos	2-chloro-1(2,4-dichlorophenyl)vinyl diethyl phosphate	359.6	145 (23)	0.530 (20)	3.8
Chlormephos	S-choromethyl O,O-diethyl phosphorodithioate	234.7	60	7600 (30)	
Chlorphoxim	2-(2-chlorophenyl)-2(dietoxyphosphinothioxyloxyimino)acetonitrile	332.7	1.7	< 1 (20)	
Chlorpyrifos	*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate	350.6	2 (25)	2.5 (25)	5.0
Chlorpyrifos-methyl	*O,O*-dimethyl *O*-3,5,6-trichloro-2pyridyl phosphorothioate	322.5	4 (24)	5.6 (25)	4.3
Chlorthion	*O,O*-dimethyl *O*-(3-chloro-4-nitrophenyl)phosphorothioate	297.5			
Chlorthiophos	*O*-2,5-dichloro-4-(methylthio)phenyl *O,O*-diethyl phosphorothioate	361.2	0.3	0.53 (25)	
Coroxon, Coralox	*O*-3-chloro-4-methyl-2-oxo-2*H*-1-benzopyran-7-yl *O,O*-diethyl phosphate	346	ins.		
Coumaphos	*O*-3-chloro-4-methyl-2-oxo-2*H*-chroment-7-yl *O,O*-diethyl phosphorothioate	362			
Coumithoate	*O*-(7,8,9,10-tetrahydro-6-oxo-6*H*-dibenzo[*b,d*] pyran-3-yl) *O,O*-diethyl phosphorothionate	368	ins.		

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Dioxathion	*S,S'*-(1,4-dioxane-2,3-diyl) *O,O,O',O'*-tetraethyl di(phosphorodithioate)	456.5	Ins.	Neg.	
Disulfoton	*O,O*-diethyl *S*-2-ethylthioethyl phosphorodithioate	274.4	25	24 (20)	4.0
Ditalimfos	*O,O*-diethyl phthalimidophosphonothioate	299.29	133	93 (100)	
Edifenphos	*O*-ethyl *S,S*-diphenyl phosphorodithioate	310.4	56	13 (20)	
EPBP	*O*-2,4-dichlorophenyl O-ethylphenylphosphonothioate	347.2	ins.	509000 (200)	
EPN	*O*-ethyl *O*-4-nitrophenyl phenylphosphonothioate	323.3	Ins.	0.126 (250	
Ethion	*O,O,O',O'*-tetraethyl *S,S'*-methylene bis(phosphorodithioate)	384.5	Sparingly	0.2 (25)	5.1
Ethoprophos	*O*-ethyl *S,S*-dipropyl phosphorodithioate	242.3	750	46.5 (26)	
Etrimfos	*O*-6-ethoxy-2-ethylpyrimidin-4-yl *O,O*-dimethyl phosphorothioate	292.3	40	6.5 (20)	
Famphur	O-4-dimethylsulphamoylphenyl O,O-dimethyl phosphorothioate	325.3	sparing.		
Fenamiphos	ethyl 4-methylthio-*m*-tolyl isopropylphosphoramidate	303.4	700	0.133 (30)	3.2
Fenchlorphos, Ronnel	*O,O*-dimethyl *O*-2,4,5-trichlorophenyl phosphorothioate	320			4.8
Fenitrothion	*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate	277.2	30	18 (20)	3.4
Fensulfothion	*O,O*-diethyl *O*-4methylsulphinylphenyl phosphorothioate	308.3	1540		2.2

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Formothion	*S*-(*N*-formyl-*N*-methylcarbamoylmethy) *O,O*-dimethyl phosphorodithioate	257.3	2600	0.113 (20)	
Glyphosate	*N*-(phosphonomethyl)glycine	169.1	12000	Negl.	
Heptenophos	7-chlorobicyclo[3.2.0]hepta-2,6-dien-6-yl dimethyl phosphate	250.6	2200	65 (15)	
IBP	*S*-benzyl *O,O*-di-isopropyl phosphorothioate	288.3	1000		
Iodofenphos	*O*-2,5-dichloro-4-iodophenyl *O,O*-dimethyl phosphorothioate	413.	<2	0.106 (20)	5.2
Iprobenfos	*S*-benzyl *O,O*-di-isopropyl phosphorothioate	288.3	1000	0.247 (20)	
IPSP	*S*-ethylsulphinylmethyl *O,O*-di-isopropyl phosphorodithioate	304.4	1500 (15)	2 (27)	
Isazofos	*O*-5-chloro-1-isopropyl-1*H*-1,2,4,-triazol-3-yl *O,O*-diethyl phosphorothioate	313.7	250	4.3 (20)	
Isofenphos	*O*-ethyl *O*-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate	345.4	24	0.53 (20)	4.1
Isothioate	*S*-2-isopropylthioethyl *O,O*-dimethyl phosphorodithioate	260.4	97	293 (20)	
Isoxathion	*O,O*-diethyl *O*-5-phenylisoxazol-3-yl phosphorothioate	313.3	1.9	<0.133 (25)	4.58
Lepthophos	*O*-4-bromo-2,5-dichlorophenyl *O*-methyl	410			5.9

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Mecarbam	*S*-(*N*-ethoxycarbonyl-*N*-methylcarbamoylmethyl) *O,O*-diethyl phosphorodithioate	329.4	<1000	Neg.	
Menazon	S-4,6-diamino-1,3,5-triazin-2-ylmethyl O,O-dimethyl phosphorodithioate	281			
Methacrifos	methyl (*E*)-3(dimethoxyphosphinothioyloxy)-2-methacrylate	240.2	400	160 (20)	
Methamidophos	*O,S*-dimethyl phosphoramidothioate	141.1	2000000	40 (30)	
Methidathion	*S*-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl *O,O*-dimethyl phosphorodithioate	302.3	240	0.13 (20)	2.4
Mevinphos	2-methoxycarbonyl-1-methylvinyl dimethyl phosphate	224.1	Misc.	17 (20)	
Monocrotophos	dimethyl (*E*)-1-methyl-2-(methylcarbamoyl)vinyl phosphate	223.2	1000000	9 (20)	
Naled	1,2-dibromo-2,2-dichloroethyl dimethyl phosphate	380.8	Ins.	266 (20)	
Omethoate	*O,O*-dimethyl S-methylcarbamoylmethyl phosphorothioate	213.2	Misc.	3.2 (20)	
Oxydemeton-methyl	*S*-2-ethylsulphinylethyl *O,O*-dimethyl phosphorothioate	246.3	Misc.	3.8 (20)	
Oxydeprofos	*S*-2-ethylsulphinyl-1-methylethyl *O,O*-dimethyl phosphorothioate	260.3	Sol.	0.625 (20)	
Parathion	*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate	291.3	24	5 (20)	3.8

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Phenthoate	*S*-α-ethoxycarbonylbenzyl *O,O*-dimethyl phosphorodithioate	320.4	11	5 (40)	4.31
Piperophos	*S*-2-methylpiperidinocarbonylmethyl *O,O*-dipropyl phosphorodithioate	353.5	25	0.032 (20)	
Pirimiphos-ethyl	*O*-2-diethylamino-6-methylpyrimidin-4-yl *O,O*-diethyl phosphorothioate	333.4	< 1	39 (25)	4.8
Pirimiphos-methyl	*O*-2-diethylamino-6-methylpyrimidin-4-yl *O,O*-dimethyl phosphorothioate	305.3	5	15 (30)	4.2
Phorate	*O,O*-diethyl *S*-ethylthiomethyl phosphorodithioate	260.4	50	110 (20)	3.8
Phosalone	*S*-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl *O,O*-diethyl phosphorodithioate	367.8	10	Neg.	4.4
Phosdiphen	bis(2,4-dichlorophenyl) ethyl phosphate	416.0	0.7	66 (20)	
Phosfolan	diethyl 1,3-dithiolan-2-ylidenephosphoramidate	255.3	650000		
Phosmet	*O,O*-dimethyl *S*-phthalimidomethyl phosphorodithiate	317.3	25	133 (25)	2.8
Phosphamidon	2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate	299.7	Misc.	3.3 (200)	
Phoxim	*O,O*-diethyl α-cyanobenzylideneamino-oxyphosphonothioate	298.3	7	10 (20)	4.4
Profenofos	*O*-4-bromo-2-chlorophenyl *O*-ethyl *S*-propyl phosphorothioate	373.6	20	1.3 (20)	
Propaphos	4-(methylthio)phenyl dipropyl phosphate	304.3	125		

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
Propetamphos	(*E*)-*O*-2-isopropoxycarbonyl-1-methylvinyl *O*-methyl ethylphosphoramidothioate	281.3	110	1.9 (20)	
Prothiofos	*O*-2,4-dichlorophenyl *O*-ethyl *S*-propyl phosphorodithioate	345.2	1.7	< 1(20)	
Prothoate	*O,O*-diethyl *S*-isopropylcarbamoylmethyl phosphorodithioate	285.4	2500	13 (40)	
Pyrazophos	*O*-6-ethoxycarbonyl-5-methylpyrazolo[1,5-a]pyrimidin-2-yl *O,O*-diethyl phosphorothioate	373.4	4.2	0.22 (20)	
Pyridafenthion	*O,O*-diethyl-*O*-[2-phenyl-3(2*H*)-pyridazinone-6-yl] phosphorothioate	340.3	ins.		
Quinalphos	*O,O*-diethyl *O*-quinaxalin-2-yl phosphorothioate	298.3	22	0.346 (20)	
Stirofos	*O,O*-diethyl *O*-2-chloro-1-(2,4,5-trichlorophenyl)ethenyl phosphate	364	11		
Sulfotep	*O,O,O',O'*-tetraethyl dithiopyrophosphate	322.3	25	22 (20)	
Sulprofos	*O*-ethyl *O*-4-(methylthio)phenyl *S*-propyl phosphorodithioate	322.4	< 5	< 0.1(20)	
Temephos	*O,O,O',O'*-tetramethyl *O,O'*-thiodi-p-phenylene bis(phosphorothioate)	466.5	ins.		5.9
TEPP	tetraethyl pyrophosphate	290.2	misc.	21 (20)	
Terbufos	*S*-tert-butylthiomethyl *O,O*-diethyl phosphorodithioate	288.4	4.5	35 (26)	4.5
Tetrachlorvinphos	(*Z*)-2-chloro-1(2,4,5-trichlorophenyl)vinyl dimethyl phsophate	366.0	11		

Common name	Chemical name (IUPAC)	M.W.	Sol. (mg/L) at 20°C.	Vapour Pressure (mPa)[a]	Log K_{ow}[b]
O,O,O',O'-tetrapropyl dithiopyrophosphate	*O,O,O',O'*-tetrapropyl dithiopyrophosphate	378.4	30	13 (25)	
Thiomethon	*S*-2-ethylthioethyl *O,O*-dimethyl phosphorodithioate	246.3	200	20 (20)	
Thionazin	O,O-diethyl O-pyrazin-2-yl phosphorothioate	248.2	1140	400 (30)	
Tolclofos-methyl	*O*-2,6-dichloro-p-tolyl *O,O*-dimethyl phosphorothioate	301.1	0.4	57 (20)	
Triamiphos	5-amino-3-phenyl-1H-1,2,4-triazol-1-yl-N,N,N',N'-tetramethylphosphonic diamide	294			
Triazophos	*O,O*-diethyl *O*-1-phenyl-1*H*-1,2,4-triazol-3-yl phosphorothioate	313.3	35	0.39 (30)	3.5
S,S,S-tributyl phosphorotrithioate	*S,S,S*-tributyl phosphorotrithioate	314.5	2.3		
Tributyl phosphorotrithioite	Tributyl phosphorotrithioite	298.5	Sparing.		
Trichlorfon	dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate	257.4	154000	1 (20)	0.43
Trichloronate	*O*-ethyl *O*-2,4,5-trichlorophenyl ethylphosphonothioate	333.6	50	2 (20)	5.2
Vamidothion	*O,O*-dimethyl *S*-2-(1methylcarbamoylethylthio)ethyl phosphorothioate	287.3	4000000	Neg.	

a: Temperature at which the vapour pressure has been measured is given in brackets
b: From Bowman and Sans, 1983 and OECD, 1989.