Parameters affecting microwave-assisted extraction of organophosphorus pesticides from agricultural soil

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Abstract

This work describes an optimised method for the determination of six representative organophosphorus pesticides (OPPs) (diazinon, parathion, methyl pirimiphos, methyl parathion, ethoprophos, and fenitrothion) in agricultural soils. The method is based on microwave-assisted extraction using a water–methanol modified mixture for desorption and simultaneous partitioning on *n*-hexane (MAEP), together with gas chromatography–flame photometric detection (GC–FPD). To improve GC–FPD signals (peak intensity and shape) olive oil was used effectively as a "matrix mimic". The optimisation of the extraction method was achieved in two steps: an initial approach through experimental design and principal component analysis where recovery of compounds using a water–methanol mixture ranged from 54 to 77%, and the second one by studying the addition of KH_2PO_4 to the extracting solution where recoveries were significantly increased, molecular replacing of OPPs from adsorption sites by phosphate being the probable extraction mechanism. Under optimised conditions, recoveries of pesticides from different soils were higher than 73%, except for methyl parathion in some soils, with SD equal or lower than 11% and detection limits ranging from 0.004 to 0.012 $\mu g\, g^{-1}$. The proposed method was used to determine OPPs in soil samples from different agricultural zones of Chile.

Keywords: Microwave-assisted extraction; GC–FPD; Organophosphorus pesticides; Soils; Chemometric approach; KH_2PO_4 effect

1. Introduction

Organophosphorus pesticides (OPPs) have been extensively used for agricultural purposes for the last five decades, providing well-characterized and cost-effective treatments to prevent, repel or mitigate the effects of pest on a wide range of crops. As a consequence, these organic compounds are frequently found in soil and other environmental matrices, constituting an animal and human health hazard. Therefore, it is necessary to monitor their residues regularly through analytical methods which combine short analysis time, sufficient selectivity and sensitivity.

Analysis of these compounds in solid environmental matrices by gas chromatography (GC) requires sample preparation to extract the contaminant from the sample, which is usually tedious and time-consuming because of the matrix complexity. Traditional fluid-phase partitioning methods to extract organic compounds from soils include Soxhlet and mechanical shakeout. However, these techniques are time- and/or solvent-consuming. Newer extraction techniques are mainly instrumental and performed under elevated pressure and/or temperature. These techniques comprise supercritical fluid extraction (SFE), pressurised liquid extraction (PLE) and microwave-assisted extraction (MAE) [1–4]. SFE and PLE are selective and non-solvent-consuming techniques; however, high equipment cost, the large number of parameters to optimise and possible restrictor blockage are their drawbacks.

Microwave-assisted extraction is well suitable for routine analysis and offers a great reduction in time and solvent consumption, and a high throughput of samples. Nevertheless, since MAE is quite exhaustive, the extract usually contains interfering species that require clean-up prior to chromatographic analysis. The use of non-polar solvents reduces the co-extraction effect; however, efficiency is also reduced because the solvent must possess a dipole to transfer microwave energy. Water has been used in MAE to extract organic compounds having different polarities from solid samples, including triazines from

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soils [5] and organochlorine pesticides from medicinal plants [6]. However, the required clean-up to eliminate the co-extracted polar interferences, the non-compatibility of aqueous extract with GC techniques and the low extraction efficiency towards less hydrophilic compounds are the principal disadvantages. To overcome these limitations in a previous study we have optimized a microwave-assisted extraction using water–acetonitrile mixture and simultaneous partitioning on *n*-hexane (MAEP), for determining halogenated pesticides in soils [7].

In this work, we propose MAEP of representative OPPs from soils using a water–methanol–KH_2PO_4 mixture for desorption, coupled with flame photometric detection. To the author's knowledge, this is the first study that presents the use of phosphate to assist the extraction of OPPs from soils. The optimisation of multi-residue extraction was performed through experimental design and PC analysis approach, which allow to reduce the number of responses to be analyzed and then to choose the adjustments of factor that maximise that component [8,9]. A previous optimisation of the chromatographic analysis quality was also carried out. Soil samples with different physicochemical properties containing ageing residues of pesticides were used to assess the applicability of the method. The proposed method presents advantages as compared to other instrumental or conventional methods: it is a very simple and low solvent-consuming technique, without any additional clean-up step and effective to extract OPPs actually adsorbed on different types of soils at residue levels. Finally, we report the results of applying the method to real samples from different agricultural zones of Chile.

2. Experimental

2.1. Chemicals and reagents

The pesticides used (ethoprophos, diazinon, methyl pirimiphos, methyl parathion, fenitrothion and parathion) had purity ≥98% (Supelco, ChemService). All the solvents used were residue analysis grade (Fisher). Water was purified with a NANOPure system (Barnstead Thermolyne). KH_2PO_4 used had purity ≥99.5% (Merck). Triphenylphosphate (TPP Aldrich) was used as an internal standard for GC–FPD determinations. Stock solutions were prepared in acetone at 1 g L^{-1}. Working standard solutions were diluted with hexane and with water for spiking purposes. Olive oil was purchased in a local supermarket.

2.2. Chromatographic analysis

2.2.1. GC–FPD

A Hewlett-Packard (Agilent; Little Falls, DE, USA) Model 5890 Series II gas chromatograph equipped with split/split less injector, an FPD and HP 3395 integrator was employed. An HP Ultra 2 capillary column (25 m × 0.2 mm i.d., 0.33 μm film thickness) was used. Helium and nitrogen (99.995%) were selected as carrier and auxiliary gas, respectively. Pesticides were separated and determined under the following conditions: injector temperature, 250 °C; detector temperature, 280 °C; column temperature program, 70 °C, held for 2 min; increased at a rate of 40 °/min up to 230 °C; held for 1 min; increased at the rate of 5 °C/min up to 280 °C; held for 1 min; increased at 40 °C/min up to 290 °C and held for 1 min. A 1-μL volume of the extract was injected in the split less mode (2 min purge). Carrier gas flow in the column was 0.65 mL min^{-1}; H_2, 75 mL min^{-1}; and air, 100 mL/min were used as combustion gases. Under these conditions, the pesticides and internal standard (TPP) were well resolved in a run time of 19 min.

2.2.2. GC–MS/MS

A Varian model CP-3800 gas chromatograph fitted with a Saturn 2200 ion trap mass spectrometer from Varian Instruments was employed. It was equipped with a CP-8400 autosampler and a split/splitless temperature-programmable injector port operated in the splitless mode. The ion trap mass spectrometer operated in the electron impact (EI) mode and the MS/MS option was used. The temperatures for the manifold, transfer line and trap were 60, 280 and 200 °C, respectively. The specific MS/MS conditions for analysis of real soil samples were: precursor ion (*m*/*z*) 158 and 291, product ions (*m*/*z*) 113.7 + 129.7 and 234.9 + 154.8, excitation amplitude 35 and 65 V, for ethoprophos and parathion, respectively. Gas chromatography was performed under the same conditions used in GC–FPD.

2.3. Soil samples

Recovery and optimisation studies were carried out using sieved samples (2 mm mesh) of three soils with diverse physicochemical properties (Table 1) collected (0–20 cm depth) in different agricultural zones in Chile: Pocuro (PCR), Quillota (QTA) and Vilcún (VLC). Belonging soils to other agricultural zones of North and South of Chile were sampled in a similar way, homogenised by grinding with a mortar and pestle, and analysed with the proposed method (samples 1–5 in Table 1).

2.4. Spiking of soil samples

As the matrix spike can be used to accept or reject a method, one should be careful in choosing the spiking procedure. Since sorption of non-ionic organic compounds in field conditions is principally due to a partitioning process between an aqueous soil solution and organic matter [10,11] and adsorption

Table 1
Physico-chemical characteristics of soils

Soil	OM (%)	pH	% Clay	% Silt	% Sand	Texture
VLC	13.4	6.3	32.7	33.0	34.3	Clay loam
QTA	3.1	7.4	15.8	54.1	30.1	Silt loam
PCR	1.8	7.2	17.5	50.7	31.8	Silt loam
1	1.3	7.7	10.0	40.0	50.0	Loam
2	10.9	5.6	0	30.0	70.0	Sandy loam
3	28.0	5.6	20.0	40.0	40.0	Loam
4	0.5	7.4	0	5.0	95.0	Sand
5	3.3	7.4	0	20.0	80.0	Loamy sand

on clay surfaces [12], samples were contaminated through a "batch" equilibrium method by addition of an aqueous solution of pesticides to soils using a low water–soil ratio and, subsequently, dry processing. To this end, 20 g of QTA soil (medium content in organic matter) was equilibrated with 10 mL of an aqueous standard solution at a proper concentration to obtain 0.025–0.1 $\mu g\,g^{-1}$ for ethoprophos, diazinon and methyl pirimiphos, and 0.05–0.2 $\mu g\,g^{-1}$ for methyl parathion, fenitrothion and parathion. The mixture was shaken for 2 h and subsequently dried at 30 °C overnight, homogenised by grinding with a mortar and pestle and stored at −20 °C until microwave extraction. The residual moisture content was also determined by drying a spiked-soil sample at 105 °C overnight. All spiked soils extracted under optimal conditions were obtained through this procedure.

2.5. Microwave-assisted extraction and partitioning (MAEP) method

For microwave-assisted extraction, a Milestone (Sorisole, Bergamo, Italy) MLS 1200 MEGA high-pressure microwave oven extraction system equipped with an exhaust module EM-45/A was used.

Soil samples were accurately weighed (1 g) and transferred to the TFM microwave extraction vessels. Then, 1–3 mL of the extraction solution (water–acetonitrile or water–methanol, 15–75%, v/v) were added and the sample was manually shaken for homogenisation. Then, 5 mL of hexane were added over the soaked soil for partitioning, TFM vessels were covered with pressure resistant holders, and preheated for 2 min at 250 W and then for 3–15 min at 300–600 W, using the microwave oven system. After microwave irradiation, the vessels were water-cooled, opened, and the hexane was carefully transferred with a Pasteur pipette to 10 mL bottom conic tubes, and finally, rinsing the inner wall with 2 mL of hexane (The filtering of the sample was not necessary since the soil remain soaked with the extraction solution, avoiding its mixture with hexane). The extract was evaporated to dryness under nitrogen and the residue redissolved with 1 mL of hexane. Internal standard (20 μL of TPP at 5 $mg\,L^{-1}$) was added for GC–FPD analysis. Depending on each particular experiment, the volume of the extracting solution, type and content of organic modifier in this solution, time and extraction power were varied according to the corresponding experimental designs. A systematic study was also performed related to the effect of KH_2PO_4 concentration (0.01–0.05 M in the extracting solution) on the extraction efficiency.

2.6. Optimisation approach

In a preliminary study, a multilevel factorial design ($2^2 \times 3^1$) was set up to assess the effect of time (3 and 6 min), microwave power (300 and 500 W) and composition of aqueous solution (water; water–methanol 1:1 and water–acetonitrile 1:1) on partition of compounds. To this end an aqueous solution (2 mL) containing diazinon and methyl pirimiphos at 0.25 $\mu g\,mL^{-1}$ and parathion and methyl parathion at 0.5 $\mu g\,mL^{-1}$ was heated in the microwave oven, in contact with 5 mL *n*-hexane. Subsequently, a fractional factorial design (FFD, 2^{5-1}) was developed to assess the effect of five experimental factors (power and time of extraction, type and amount of organic modifier and volume of extracting solution) on the extraction efficiency. An additional central composite design (CCD) was set up to optimise the extraction method through evaluation of the response surface. To assess the above-described experiments we used PCA to simplify and factorise the OPPs response matrices. This previous analysis permits to model the systematic variance of the responses and leave noise unmodelled. Then, principal component score vectors are used as responses in the experimental designs. Statistical software (Statgraphics Plus v 5.1 for Windows, Rockville, MD) was used to build the experimental design and to analyse data from experimental values. The effect of KH_2PO_4 concentration on extraction efficiency was studied independently.

3. Results and discussion

3.1. Chromatographic analysis

GC–FPD analysis of methyl parathion and parathion showed low and irreproducible responses. This effect was smaller for diazinon and methyl pirimiphos. Moreover, in the case of methyl parathion, poor peak shapes were observed. This is a common problem in gas chromatography applications and is due to undesired interactions with active sites in the inlet and column when no matrix is present. Significant peak quality improvement can be obtained when matrix components are present to fill active sites, thus reducing analyte interactions and increasing their transference to the chromatographic column. This effect has been called "matrix-induced chromatographic response enhancement" [13]. A variety of compounds employed as "matrix mimics" have been evaluated by some authors to improve the quality of GC analysis [14–17]. Good results have been reported using L-gulonic acid γ-lactone [14,15], corn oil [16] and olive oil [17]. Due to its solubility in hexane and ready availability, we selected olive oil as a "matrix mimic" to improve our chromatographic analysis. Olive oil at 0.3% (v/v) had a significant effect on peak shape and intensity, particularly for methyl parathion and parathion. A higher content in olive oil did not improve the signals. In this manner, the quality parameters of GC–FPD were established under this condition. The instrumental limit of quantification was obtained from a calibration curve containing the corresponding internal standard, olive oil at 0.3% (v/v) and the compounds at five concentration levels between 2.5 and 25 $\mu g\,L^{-1}$ for diazinon and methyl pirimiphos and 5.0 and 50 $\mu g\,L^{-1}$ for methyl parathion and parathion. Except for methyl parathion ($r = 0.981$), the correlation coefficients were higher than 0.998. The instrumental limit of quantification (concentration equivalent to 10 times the standard error of calibration curve) was 3.0 $\mu g\,L^{-1}$ for diazinon and methyl pirimiphos, 11 $\mu g\,L^{-1}$ for parathion, and 37 $\mu g\,L^{-1}$ for methyl parathion. Seeing that in the MAEP experiments, the extracts obtained were clean and no evident matrix was present, olive oil was added to match the calibration matrix.

3.2. Preliminary study on partitioning efficiency

This study was carried out to evaluate the partition of OPPs between aqueous solution and hexane after the microwave process. Partitioning on *n*-hexane of diazinon and methyl pirimiphos was not affected by experimental factors, and recoveries higher than 90% were observed in all experiments. Power and time had a positive effect on methyl parathion partitioning, reaching quantitative trapping at 500 W and 6 min, independent of aqueous solution composition. Parathion partition was positively affected by interaction between time of extraction and solution composition. This means that for quantitative trapping of parathion from a water–organic modifier mixture, 6 min is required as irradiation time. To evaluate differences between chromatographic responses of compounds dissolved in hexane and those submitted to MAEP, a comparison through a least square test with five standards was performed. Non-systematic differences were observed, since the (1,0) point was included in the confidence interval of slope and intercept for all compounds. Results show that, under appropriate experimental conditions (500 W and 6 min), transfer of compounds from aqueous mixture to n-hexane is not a limiting step in the method of extraction proposed.

3.3. Screening study of MAEP method

In a preliminary extraction of spiked soil under no optimised conditions, the lowest recoveries were obtained from Quillota soil. Then, screening and optimisation of extraction was carried out using this soil. In MAEP, five factors were defined to evaluate their contribution to the extraction method. A 2^{5-1} fractional factorial design (resolution V) was used to evaluate the effects of single factors and its interactions (19 experiments including 3 duplicates), with the PC scores as a single response. The first principal component obtained from standardized recovery values, accounts for 86% of the total variance of the four pesticide recovery data, and showed that diazinon, methyl pirimiphos and parathion have similar recoveries under a set of experimental conditions, whereas the recovery of methyl parathion is different. The ANOVA of regression of experimental factors in response to PC1 scores showed that volume of extracting solution, type and amount of modifier in the water and time of extraction had a significant negative effect on MAEP efficiency. Several interactions of these factors also had a significant effect. Power was not a significant factor, although it was included in significant interactions with volume of extracting solution and type of modifier. This indicates that extraction increases if greater power is applied with smaller volume of extracting solution. Excluding power from the fitted model, R^2 value adjusted for numbers of degrees of freedom was 0.9066 and *p*-value for lack of fit, 0.1512 (at the 95% confidence level). For the ANOVA of regression for PC2 no significant factors were observed.

3.4. Optimisation of MAEP method

Time of extraction and amount of modifier were simultaneously optimised through a rotatable central composite design comprising a 2^2 full factorial design, 4 added axial points and 2 central points. According to the preliminary study on partitioning efficiency and screening experiment, volume of extracting solution and power were fixed at 1 mL and 500 W, respectively. Methanol was selected as the organic modifier and spiked QTA soil was used for optimisation. The first principal component accounts for 74% of the total variance and its scores are principally determined by diazinon, methyl pirimiphos and parathion recoveries. The second principal component accounts for 24% of the total variance and is mainly determined by methyl parathion recovery. PC1 score response surface (Fig. 1A) show that optimum conditions are an extraction time of 10 min and methanol percentage of 45% (v/v). Instead PC2 score response surface (Fig. 1B) show maximal response at methanol percentage higher than 50% (v/v). The models as fitted explain 77% of the variability in PC1 score and only 48% in PC2 score. Thus, the optimal conditions predicted are more reliable from the PC1 score response surface. The optimal extraction conditions retained were 10 min at 500 W using 1 mL of extracting solution with 50% (v/v) methanol content.

However, even under these optimal conditions, recoveries of compounds from QTA soil were lower than 77%. These poor recoveries are probably due to a strong adsorption of organophosphorus compounds on soil components which make extraction difficult. In fact, the adsorption parameters obtained from the empirical Freundlich model [18], K_f and $1/n$, for these compounds in Quillota soil ranged from 56 to 110 mL g^{-1} and 0.38 to 0.58, respectively. These values reflect high sorption capacity with contribution of heterogeneous sites in organic matter and clay minerals. Sorption of organophosphorus pesticides on clay minerals has already been described [19–21] and

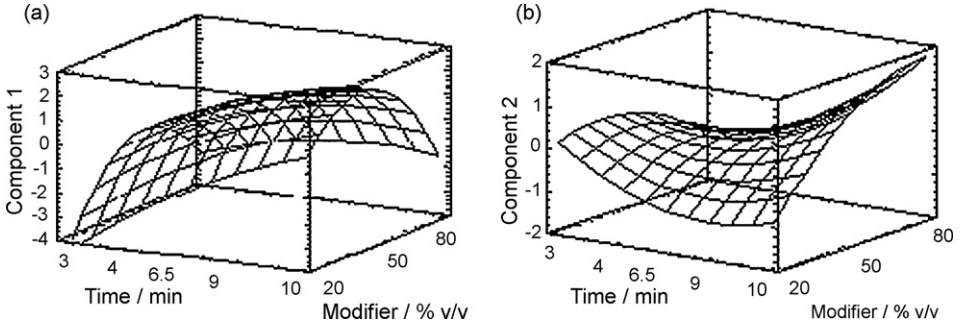

Fig. 1. Optimisation of the MAEP method. Response surfaces obtained from the regression on (a) the first and (b) second principal component scores.

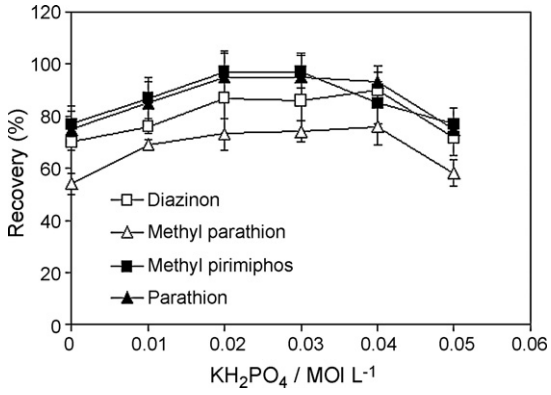

Fig. 2. Effect of KH_2PO_4 concentration on the extraction efficiency.

is responsible for the low mobility of some of these compounds in soils.

3.5. Effect of ortho-phosphate on extraction efficiency of MAEP

Some authors have observed that after addition of KH_2PO_4, the K_f values of glyphosate on sandy loam soil were 78–98% lower than with the $CaCl_2$ treatments; showing that ortho-phosphate competed with this organophosphorus pesticide for available sorption sites [22]. According to these facts, it was expected that ortho-phosphate could replace the OPPs from the sorption sites in soil and thus increase the efficiency of extraction so far obtained. Then, Quillota soil spiked at 0.05 $\mu g\,g^{-1}$ with diazinon and methyl pirimiphos and 0.1 $\mu g\,g^{-1}$ with parathion and methyl parathion was extracted with a mixture of water–methanol 1:1 and KH_2PO_4 at 0.01, 0.02, 0.03, 0.04 and 0.05 M to evaluate the phosphate-replacing effect. Results are shown in Fig. 2. As the concentration of KH_2PO_4 was increased, recoveries of all compounds increased to a plateau reached between 0.02 and 0.04 M, decreasing from then on. At these KH_2PO_4 concentrations, recoveries were higher than 85%, except for methyl parathion, with a maximum recovery near 75%. At higher concentration, the extraction efficiency diminished probably due to changes in the adsorption equilibrium increasing the amount of bound residues. Thus, 0.02 M KH_2PO_4 was selected as optimum to extract the OPPs compounds.

3.6. Analytical performance of the MAEP and GC–FPD method

The method was applied to determine six OPPs at residual levels in three different soils at two ageing periods. To this end, QTA, PCR and VLC soil samples were spiked at two levels: 0.025 and 0.05 $\mu g\,g^{-1}$ with ethoprophos, diazinon and methyl pirimiphos and 0.05 and 0.1 $\mu g\,g^{-1}$ with methyl parathion, fenitrothion and parathion, stored at −20 °C and extracted at days 3 and 15 (soils with organic matter content higher than 10% were extracted with 2 mL of extracting solution). Results are summarised in Table 2. Average pesticide recoveries from soils at day 3 varied from 73 to 113% with SD equal or lower than 11%. Similar recoveries were obtained from soils at day 15 and at lower concentration. In the case of PCR soil, a decrease in recoveries was observed for methyl parathion. Decreasing recoveries resulting from ageing of matrices is a well-known fact and involves sorption at remote microsites within the soil matrix, representing bound residues [23]. Degradation of compounds was discarded since spiked soils were stored dry, in the dark at −20 °C.

As a result of the simultaneous cleanup by partitioning during the extraction process, a colourless organic solvent phase was recovered and no interference was observed in the determination of pesticides by GC–FPD, even in a soil with higher organic matter content (VLC soil, 13.4%). Fig. 3 shows the chromatogram from VLC soil extract obtained using optimum extraction conditions. Once MAEP and GC–FPD was applied, detection and quantification limits for each analyte were calculated (corresponding to 3 and 10 times the standard error of the signal obtained for six QTA soil extracts). LOD values ranged

Table 2
Percent recoveries ($n = 3$) ± standard deviations for spiked soils obtained with the optimised MAEP-GC–FPD method

	Spike level ($\mu g\,g^{-1}$)	Recovery (%)							
		PCR		QTA		VLC		Soil 1	Soil 3
		3 days	15 days	3 days	15 days	3 days	15 days	15 days	15 days
Ethoprophos	0.05	82 ± 2	74 ± 3	93 ± 2	103 ± 5	113 ± 11	95 ± 9	–	–
	0.025	–	81 ± 6	–	98 ± 7	–	92 ± 8	84 ± 4	80 ± 2
Diazinon	0.05	94 ± 2	83 ± 8	87 ± 6	91 ± 7	96 ± 7	85 ± 7	–	–
	0.025	–	88 ± 8	–	100 ± 10	–	83 ± 7	91 ± 9	82 ± 2
Methyl parathion	0.1	84 ± 8	56 ± 6	73 ± 6	67 ± 4	89 ± 7	86 ± 7	–	–
	0.05	–	66 ± 6	–	75 ± 4	–	93 ± 5	81 ± 3	75 ± 5
Methyl pirimiphos	0.05	104 ± 8	87 ± 8	97 ± 8	97 ± 6	102 ± 10	88 ± 8	–	–
	0.025	–	98 ± 9	–	101 ± 2	–	85 ± 7	85 ± 2	89 ± 5
Fenitrothion	0.1	93 ± 8	95 ± 8	91 ± 9	95 ± 8	105 ± 10	93 ± 7	–	–
	0.05	–	81 ± 8	–	96 ± 2	–	92 ± 10	94 ± 6	92 ± 4
Parathion	0.1	103 ± 9	82 ± 3	95 ± 9	98 ± 8	110 ± 10	93 ± 7	–	–
	0.05	–	94 ± 2	–	91 ± 2	–	91 ± 9	89 ± 2	95 ± 9

Table 3
Analytical features of the MAEP–GC–FPD method obtained under optimized conditions (LOD and LOQ 3 and 10 times the standard error of the signal obtained for six QTA soil extracts)

Compound	Analytical sensitivity ($\mu g\,g^{-1}$)[a]	LOD ($\mu g\,g^{-1}$)	LOQ ($\mu g\,g^{-1}$)	Precision (RSD)
Ethoprophos	0.002	0.006	0.019	4.8
Diazinon	0.001	0.004	0.012	3.4
Methyl parathion	0.004	0.012	0.035	7.5
Methyl pirimiphos	0.002	0.006	0.018	5.1
Fenitrothion	0.003	0.008	0.025	5.9
Parathion	0.002	0.006	0.019	3.8

[a] Minimal difference in concentration detected by the method = (SD chromatographic signal/slope of calibration curve)$^{-1}$.

from 0.004 to 0.012 $\mu g\,g^{-1}$ (Table 3). This permits to quantify the compounds under study in 1 g of soil containing concentrations as low as 0.035 $\mu g\,g^{-1}$ for methyl parathion or lower for the other organophosphorus pesticides, under the optimised conditions.

3.7. Real samples analysis

Five soils from some agricultural zones of Chile were analysed under optimised conditions ($n = 3$) (soils with organic matter content higher than 10% were extracted with 2 mL of extracting solution). Only parathion (0.020 ± 0.003 $\mu g\,g^{-1}$) and ethoprohos (0.028 ± 0.003 $\mu g\,g^{-1}$) were determined in soils 2 and 5, respectively. The identity of these pesticides residues was confirmed through GC–MS/MS analysis. As OPPs were not detected in the other soils samples, two of them with physicochemical properties quite different (soils 1 and 3) were spiked at 0.025 $\mu g\,g^{-1}$ with ethoprophos, diazinon and methyl pirimiphos and 0.05 $\mu g\,g^{-1}$ with methyl parathion, fenitrothion and parathion, stored at $-20\,^{\circ}C$ and extracted after 15 days. Mean recovery of compounds ranged 75–95% with SD equal or lower than 9% (Table 2), which verify the applicability of the proposed method.

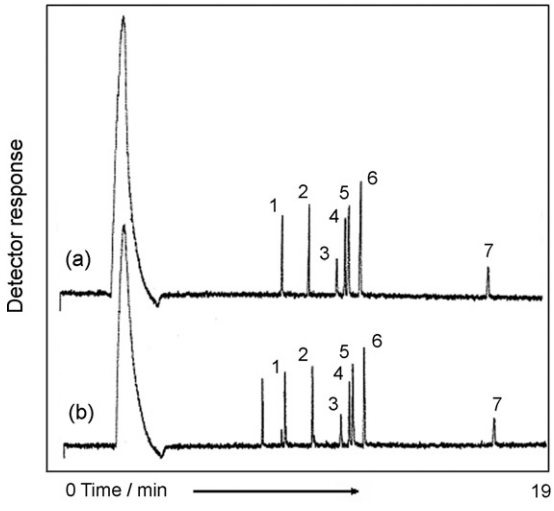

Fig. 3. GC–FPD chromatogram obtained for (a) a standard solution of pesticide mixture 0.05 $\mu g\,mL^{-1}$ ethoprophos, diazinon and methyl pirimiphos and 0.1 $\mu g\,mL^{-1}$ methyl parathion, fenitrothion and parathion. (b) A MAEP extract from VLC soil spiked at 0.05 $\mu g\,g^{-1}$ ethoprophos, diazinon and methyl pirimiphos and 0.1 $\mu g\,g^{-1}$ methyl parathion, fenitrothion and parathion. Pesticides: 1, ethoprophos; 2, diazinon; 3, methyl parathion; 4, methyl pirimiphos; 5, fenitrothion; 6, parathion and 7, TPP (internal standard at 0.1 $\mu g\,mL^{-1}$).

4. Conclusions

The MAEP and GC–FPD method is simple, selective, and sensitive to determine organophosphorus pesticides at sub $\mu g\,g^{-1}$ level in agricultural soils. Chromatographic analysis was improved through the "matrix-induced chromatographic response enhancement effect" using olive oil as a "matrix mimic". Addition of KH_2PO_4 to the water–methanol extraction mixture has permitted to increase MAEP efficiency to extract OPPs. Partitioning on hexane operating as an "in situ" cleanup process simplifies sample preparation before chromatographic analysis. The optimisation approach through principal component analysis and experimental design and recovery studies carried out with soils containing actually sorbed OPPs allowed a critical evaluation of the proposed method. By applying the method to soil samples from different agricultural zones of Chile, ethoprophos and parathion were detected in two samples. The similar recoveries and SD values obtained for the target compounds when the method developed was used for the analysis of different soil support its feasibility irrespective of the properties of the soil investigated.

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