



Multiresidue determination of organophosphorus pesticides in corn oil using solid-phase extraction with lanthanum silicate sorbent and gas chromatography

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ABSTRACT

Phosalone, malathion and diazinon were analyzed in corn oil using solid phase extraction (SPE) with lanthanum silicate as a new solid sorbent followed by gas chromatography with nitrogen phosphorus detection (GC-NPD). The efficiency of different eluents (methanol, dichloromethane, ethyl acetate, dichloromethane – ethyl acetate (1:1) and ethyl acetate – methanol (1:1)) were compared for elution of organo-phosphorus pesticides on lanthanum silicate-SPE in corn oil. Recoveries with methanol as eluent were 87% for phosalone, 95% for malathion and 69% for diazinon with standard deviations of 5-14% in the concentration range of 0.5-2 mg kg⁻¹. The limits of detection for these organophosphorus pesticides, were lower than maximum residue limits (MRLs) established by WHO/FAO. Thin layer chromatography was performed using bed of lanthanum silicate ion exchanger to ensure the existence of the pesticides residue in the SPE-extract. They were determined using gas chromatograph equipped with nitrogen phosphorus detector.

Keywords: Organophosphorus pesticides, SPE, Lanthanum silicate.

1. INTRODUCTION

Organophosphorus pesticides have become increasingly important in recent years, due to their broad spectrum of activity and relatively rapid disappearance¹. The detection of their residues in food has aroused a great deal of public concern as organo-phosphorus pesticides are used in agriculture on a large number of crops including corn. Analytical monitoring is necessary to protect the consumer from the harmful impact of pesticide residues. The common

screening methods for corn and corn oil involve initial sample preparation and multiple extractions, making them very expensive and time consuming. Solid-phase extraction (SPE) is an important technique², for sample isolation and pre-concentration. The development of small, disposable cartridge systems containing solid adsorbents has greatly speeded the extraction process prior to analysis. Interferences can be selectively washed from the column and the desired analyte recovered by solvent elution. However, new selective adsorbents are needed to

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expand the area of application of this technique. During the last two decade, new synthetic inorganic ion exchangers have been developed which show high selectivity towards certain elements³⁻⁶ and may be used as potential sorbents in SPE applications. Lanthanum silicate, a promising ion exchanger⁷ which shows unusual selectivity^{8,9} has been employed here to develop a SPE method for few organophosphorus pesticides in corn oil.

2. EXPERIMENTAL

2.1. Chemicals and Materials

Phosphorus pesticides standards, >95% purity were diazinon (GIBA-GEIGY), phosalone (RHONE-POULENC) and malathion (CHEMINOVA-HINDUSTA). Stock solutions were prepared in methanol with a pesticide concentration of 1000 mg/L and were stored in glass-stopper bottles at 4°C.

Standard working solutions of various concentrations were prepared daily by appropriate dilution of aliquots of the stock solution in methanol. All chemicals were of analytical grade or HPLC grade (E. Merck or Aldrich).

2.2. Apparatus

The equipment used in the study was a Varian model 3400 GC-NPD with HP1 (dimethyl silicon), Lida 12-port vacuum manifold apparatus, X-ray diffractometer (Seifort 3003), FT-IR spectrometer (Bomem, MB 100), pH meter (Horriba, M-12) and TLC-automatic coater (CAMAG).

2.3. Preparation of Ion-Exchanger

Lanthanum silicate was prepared⁷ by mixing the lanthanum nitrate (0.1 M) and sodium silicate (0.1 M) solutions in the volume ratio (1: 3) and the pH of the reaction mixture was adjusted to 6.33. The resulting gel material was divided into two parts S1 and S2. The sample S1 was refluxed in mother liquor at 70-74 °C for 48h whereas S2 was used without treatment. The samples filtered, washed with nano-pure water and dried in air at 50°C. The dried gel materials were finally ground and sieved.

2.4. Solid phase extraction

The corn oil samples for analysis were obtained from a local market. For the preparation of spiked samples, volumes between 50 and 100 µL of the standard working solutions were added to such sample (1 g) to give pesticide concentrations of (0.5, 1 and 2 mg kg⁻¹) before dilution with hexane. Samples were then allowed to stand at room temperature for 2 h. Solid phase extraction was performed with a 6 ml syringe barrel with polyethylene frits. The syringe barrel was packed with 500 mg lanthanum silicate (S1) ion exchanger. SPE columns were used in conjunction with a standard lida 12-port vacuum manifold apparatus. The column was conditioned with

methanol and the diluted sample solution containing organophosphorus pesticide was passed through the column. After the extraction, the SPE column was dried completely by passing air through it for few minutes. Interferences were washed with 3 mL hexane. Methanol (5mL) was used as the final eluent. The SPE-extract was collected into a graduated conical tube (15 mL) and evaporated to dryness under nitrogen. The resulting material was dissolved in methanol and analyzed by TLC and GC-NPD.

2.5. Thin layer chromatography (TLC)

TLC was performed on 20×20 cm glass plates pre-coated with lanthanum silicate ion exchanger. As described earlier in Section 2.3, a white gel was formed by mixing lanthanum and silicate salt solutions. The gel was kept overnight and washed three times with nano-pure water. The supernatant liquid was then removed completely. A sample of gel (50 mL) was mixed with calcium sulfate (10 g). This slurry was used to coat five glass plates with a 300 µm layer using an automatic TLC coater. Lanthanum silicate TLC plates were first dried at 50°C and then 110°C for two hours and stored in a dessicator. Palladium chloride solution was used as a locating reagent¹⁰.

2.6. Gas chromatographic conditions

The sample extracts were analyzed using a Varian model 3400 gas chromatograph equipped with a NP detector. An HP1 (dimethyl silicone) capillary column (30 m×0.53 mm I.D., 1.5 µm coating thickness) was used with nitrogen as the carrier gas (linear velocity=34 cm s⁻¹). The detector gas flow was hydrogen (4 mL min⁻¹), air (93.8 mL min⁻¹) and nitrogen as detector make-up (32.3 mL min⁻¹). The temperature of the injector port was 180°C. The temperature of the column was initially set at 150°C, and increased after three minutes to 250°C at a rate of 3°C min⁻¹. The temperature of the detector was 320°C. The volume of extract injected was 1µl. Figure 1 shows a chromatogram for diazinon (t_R=13.2), malathion (t_R=17.74) and phosalone (t_R=32.42) in lanthanum silicate-SPE extract of corn oil.

2.7. Fourier Transform Infrared (FT-IR) and X-Ray Diffraction (XRD).

FT-IR spectrum of lanthanum silicate ion exchanger was measured using the standard KBr method¹¹ (Figure 2). XRD analysis of S1 and S2 dried at 50°C, using nickel-filtered Cu-Kα radiation indicates that both have weak crystalline structure and S1 (refluxed sample) has a more crystalline pattern than S2.

2.8 Endurance test

To perform the endurance test¹² lanthanum silicate (100 mg) was placed in a test tube and either 10 mL of 1M or 0.1M HCl or 50 mL of 0.5M sodium hydroxide solution was added. After shaking, solvent was removed by centrifuging at 1500 rpm. The resulting residue was washed with nanopure

water and centrifuged again. Recovery was determined after the sample had been dried. Table 1 show that S1 (sample refluxed for 48 h) has a satisfactory stability in acid and base media.

2.9. Density and bulk density

These parameters were measured using by standard methods¹³. The density was $2.77\text{cm}^3\text{g}^{-1}$ and the bulk density (the density of the whole sample) was $1.46\text{cm}^3\text{g}^{-1}$. Larger bulk density implies greater mechanical stability of particles and greater stability of the chromatographic bed¹⁴.

3. RESULTS AND DISCUSSION

Some preliminary studies were carried out in order to investigate the potential of lanthanum silicate as a new sorbent in solid-phase extraction of diazinon, phosalone and malathion from corn oil.

The FT-IR spectrum of lanthanum silicate recorded in Figure 2 shows that it has a typical structure of inorganic ion-exchanger based on silicate as reported earlier⁷. The results of endurance test compared to common silica gel are recorded in Table 1 which shows that S1 (sample refluxed for 48 h) has a satisfactory stability in acid and base media.

For rapid identification of diazinon, phosalone and malathion residues from the SPE extract, chromatographic behaviours of the pesticides on TLC

bed of lanthanum silicate were studied in several solvent systems. The methanol-15% ammonia (9 : 1 volume) mixture was the best mobile phase for the separation of the malathion, phosalone and diazinon from the corn oil extract. The R_f values were malathion (0.84), phosalone (0.80) and diazinon (0.76).

For solid phase extraction, different eluents such as methanol, ethyl acetate, dichloromethane, ethyl acetate-dichloromethane (1:1 by volume) and methanol-ethyl acetate (1:1 by volume) tested following the procedure reported in section 2.4. The results are given in Table 2. Methanol produces better mean recoveries for phosalone and malathion. Detection limits were obtained by direct injection of the standard mixtures and calculated with a signal-to-noise ratio $[n=3]$ ¹⁵. Detection limits were 0.02mg kg^{-1} for phosalone, 0.016mg kg^{-1} for malathion and 0.018mg kg^{-1} for diazinon. Maximum residue limits of phosalone, malathion and diazinon in corn oil are all 0.1mg kg^{-1} ¹⁶. These are higher than the detection limits and the present method is thus useful for extraction of these organophosphorus pesticides from corn oil.

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Table 1. Endurance test for lanthanum silicate

Sample	1M HCl	0.1M HCl	0.5M NaOH	0.05M NaOH
Recovery (R%)				
S1	91.5%	93%	95.7%	97.9%
S2	97.9%	69.9%	78.5%	89.6%
Silica gel *	95.5%	96.3%	0%	73%

* The data for silica gel were given by Kawahara & coworkers¹².

Table 2. Average recoveries# (R%) and relative standard deviation (RSD, n=3) obtained from different eluents for the solid phase extraction

	CH ₃ OH		CH ₂ Cl ₂		Ethyl acetate		CH ₂ Cl ₂ -Ethyl acetate(1:1)		Methanol-Ethyl acetate(1:1)	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
Phos. *	87	14	92	11	50	9	51.3	10	48	8
Mal.	95	5	35	16	60	8	26.6	6	55	15
Diaz.	69	9	41	11	40	13	70	17	76	13

* Phos. = phosalone, Mal. = malathion and Diaz = diazinon

#: The data are the mean recoveries of triplicate measurements for corn oil samples (spiked between the concentration range of $0.5\text{-}2\text{mg kg}^{-1}$).

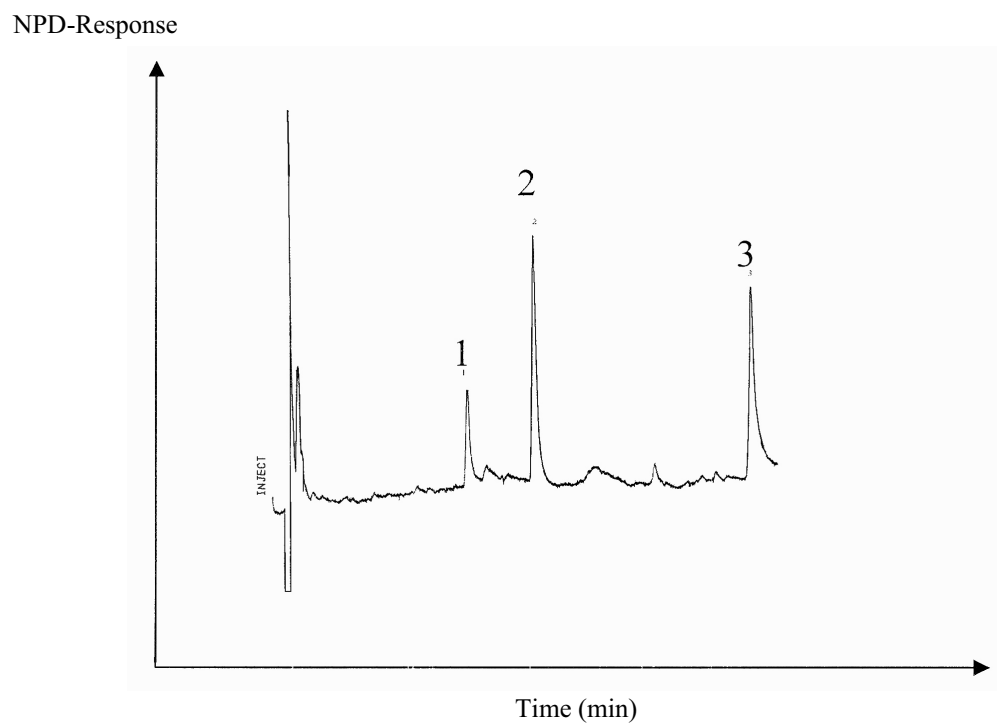


Figure 1. Gas chromatogram of an SPE-extract. 1= diazinon, 2= malathion 3= phosalone.

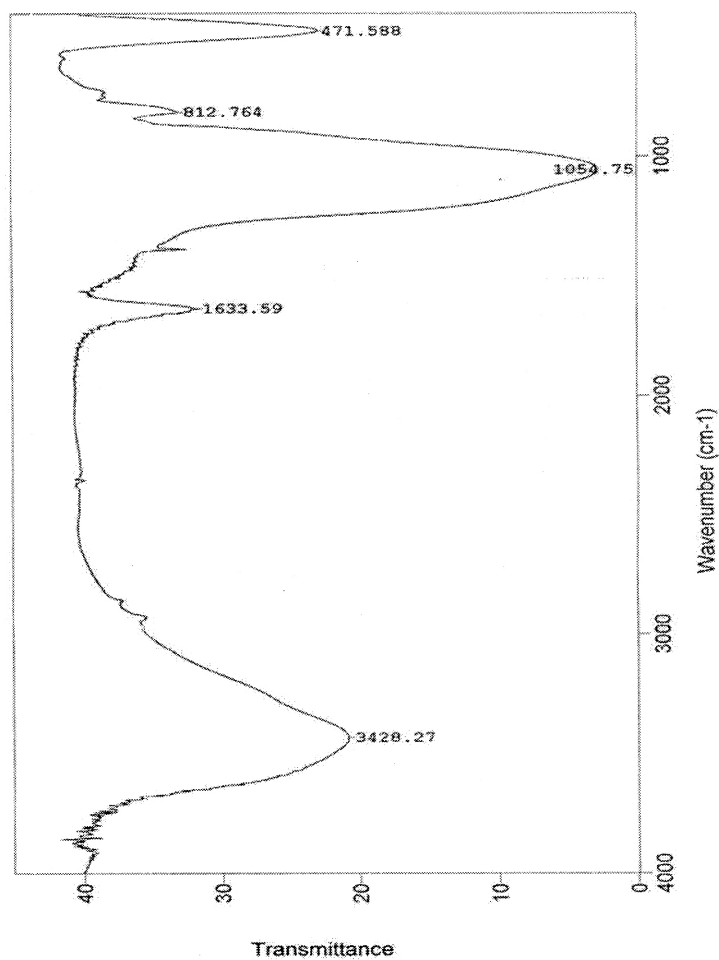


Figure 2. FT-IR spectrum of the lanthanum silicate sorbent.

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