

**MULTIRESIDUE DETERMINATION OF DIAZINON
AND ETHION IN PISTACHIO NUTS
BY USE OF MATRIX SOLID PHASE DISPERSION
WITH A LANTHANUM SILICATE CO-COLUMN
AND GAS CHROMATOGRAPHY**

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SUMMARY

Diazinon and ethion in pistachio nuts have been analyzed by use of matrix solid-phase dispersion (MSPD) followed by gas chromatography with nitrogen–phosphorus detection (GC–NPD). The efficiency of different adsorbents (C₁₈, cyano, phenyl, and amino) for MSPD of pistachio nuts was compared. Lanthanum silicate ion-exchanger was used as co-column material. Recoveries for C₁₈-MSPD co-column lanthanum silicate were 95% for ethion and 94% for diazinon with relative standard deviations of 7–13% in the concentration range 0.5–4 mg kg⁻¹. The limits of detection were 0.02 mg kg⁻¹ for ethion and 0.035 mg kg⁻¹ for diazinon; these were lower than the maximum residue limits (MRL) established by WHO/FAO. Thin-layer chromatography was performed on lanthanum silicate and lanthanum tungstate ion exchangers to ensure the pesticide residues were present in the final MSPD extract.

INTRODUCTION

The use of solid-phase extraction (SPE) in analysis requires that a sample should be in a homogenous, liquid state before addition to an SPE column or disk device [1]. A new process for the simultaneous disruption and extraction of semi-solid and solid samples was introduced in 1989 [2] and has been almost exclusively applied to the analysis of drugs, herbicides, pesticides, and other pollutants from animal tissues, fruits, and vegetables [3].

Iran is a major producer and exporter of pistachio nuts. Pesticides are widely used in the cultivation of pistachio nuts and strict control is necessary to protect the consumer from the harmful impact of pesticide residues. Common methods for screening pistachio nuts involve tissue preparation and multiple extraction, purification and concentration steps; these make analysis very expensive and time-consuming, because a large number of samples must be analyzed. The MSPD method eliminates some of the difficulties associated with other extraction procedures. During last two decades new synthetic inorganic ion-exchangers have been developed which are highly selective for some elements [4–7]; these can also serve as potential adsorbents in SPE and MSPD co-column techniques. Lanthanum silicate ion-exchanger has been used here to develop co-column MSPD for diazinon and ethion residues in MSPD extracts of pistachio nuts. This paper describes a rapid method which uses a lanthanum silicate co-column, GC–NPD, and TLC on lanthanum silicate and lanthanum tungstate as stationary phases for determination and identification of diazinon and ethion residues in MSPD extracts of pistachio nuts.

EXPERIMENTAL

Chemicals and Materials

Organophosphorus pesticides (diazinon and ethion) were supplied by the Ministry of Agriculture Research Organization (Tehran, Iran). Standard stock solutions were prepared in methanol and contained each pesticide at a concentration of 1000 mg L⁻¹; these were stored in glass-stoppered bottles at 4°C. Standard working solutions of different concentration were prepared daily by appropriate dilution of the stock solution with methanol. All chemicals were of analytical grade or HPLC grade (E. Merck or Aldrich).

Synthesis

Lanthanum silicate was prepared [7] by reaction of lanthanum nitrate (0.1 M) and sodium silicate (0.1 M) solutions, in the volume ratio 1:3, with the pH of the reaction mixture adjusted to 6.33. The resulting material was filtered, washed with nano-pure water, and dried in an air oven at 50°C. The dried material was finally ground and sieved.

Matrix Solid Phase Dispersion (MSPD)

The samples analyzed (pistachio nuts) were obtained from pistachio markets. Representative portions of sample (200 g) were ground and homogenized and 0.5-g portions were placed in an agate mortar. For preparation of spiked samples between 50 and 100 μL of the standard working solutions were added to 0.5 g sample. They were then left to stand at room temperature for 2 h. Samples were spiked with pesticides at five concentration levels 0.5, 1, 2.5, 3 and 4 mg kg^{-1} . The 0.5 g portions in the agate mortar (50 mL capacity) were gently blended with 1 g of the material to be tested (C_{18} , phenyl, cyano, and amino) for 5 min, using a pestle to produce a homogeneous mixture. This homogenized mixture was then introduced into a 6-mL syringe-barrel column, on top of lanthanum silicate ion-exchanger (0.5 g) which had previously been packed in the lower part of the syringe barrel column as an MSPD co-column. After washing of the column with hexane (7 mL), dichloromethane–ethyl acetate (50:50, v/v; 10 mL) was used for elution. The sample was eluted drop-wise by application of a slight vacuum to a Lida 12-port vacuum manifold apparatus. The eluent was collected in graduated conical tubes (15 mL) and evaporated to dryness under a stream of nitrogen. The resulting material was dissolved in methanol and analyzed by TLC and GC–NPD.

Thin-Layer Chromatography (TLC)

TLC was performed on 10 cm \times 10 cm glass plates coated with lanthanum silicate or lanthanum tungstate ion exchangers. For synthesis of lanthanum silicate, lanthanum and silicate salt solutions were mixed and a white gel was formed. The gel was kept overnight and washed three times with nano-pure water. The supernatant liquid was then removed completely. This gel (50 mL) was mixed with calcium sulfate (10 g) and the slurry obtained was used to coat five glass plates (20 cm \times 20 cm) with a 300- μm layer by means of an automatic TLC coater (Camag).

Lanthanum tungstate was prepared [8] by mixing solutions of lanthanum nitrate (0.05 M) and sodium tungstate (0.05 M) in the volume ratio 1:2 with the pH of the reaction mixture adjusted to 2–3. The white gel formed was washed three times with nano-pure water and 20 mL of the gel was mixed with 7 g calcium sulfate. This slurry was used to coat five glass plates (20 cm \times 20 cm) with a 300- μm layer by means of the automatic TLC coater. Lanthanum silicate and lanthanum tungstate TLC

plates were dried at 50°C, and then at 110°C for 2 h, and stored in desiccator.

Palladium chloride was used as a detection reagent [9].

Conditions for Gas Chromatography

The sample extracts were analyzed by use of a Varian model 3400 gas chromatograph equipped with nitrogen–phosphorus detection (NPD) and a 30 m × 0.53 mm i.d., 1.5 μm film thickness, HP1 (polydimethylsiloxane) capillary column. Nitrogen was used as carrier gas (linear velocity 34 cm s⁻¹). The detector gas (hydrogen) flow was 4 mL min⁻¹; the air flow was 93.8 mL min⁻¹ and nitrogen was used as detector make-up at 32.3 mL min⁻¹. The injector temperature was 180°C. The column temperature was programmed from 155°C to 250°C at 3° min⁻¹. The detector temperature was 320°C. The injection volume was 1 μL. Figure 1 shows the GC chromatogram obtained from diazinon ($t_R = 11.72$) and ethion ($t_R = 24.24$) in a C₁₈-MSPD co-column lanthanum silicate extract of pistachio nuts.

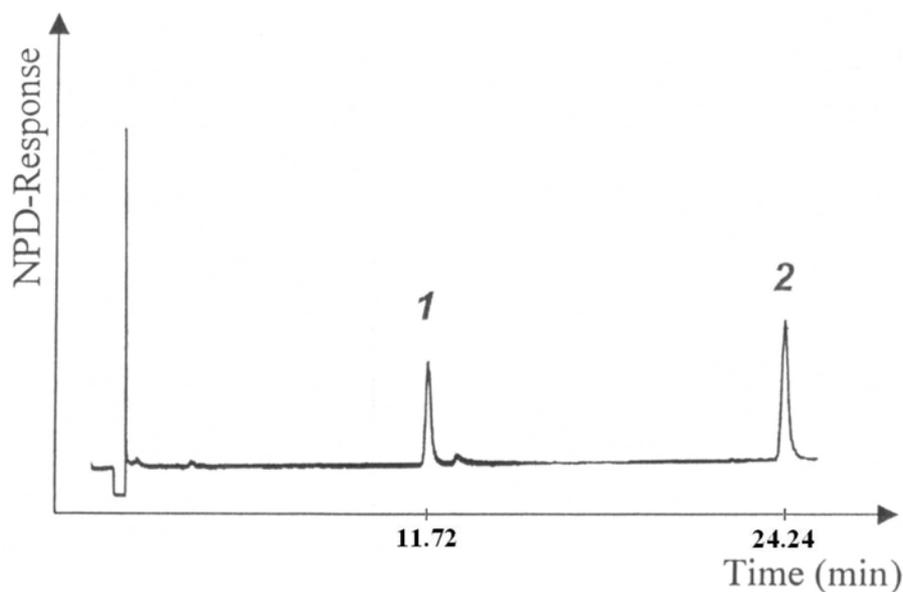


Fig. 1

Gas chromatogram obtained from MSPD extract. 1, diazinon; 2, ethion

RESULTS AND DISCUSSION

Optimization of MSPD Extraction

Different bonded phases – C₁₈, cyano, phenyl, and amino – were tested by following the procedure described above. The results are shown in Table I. These data are the mean recoveries obtained, in triplicate, from

Table I

Mean recoveries of diazinon and ethion from pistachio extract by use of different bonded phases

Pesticide	Recovery (%) from:			
	C ₁₈	Phenyl	Amino	Cyano
Diazinon	94	76	52	41
Ethion	95	73	47	45

pistachio samples spiked at concentrations in the range 0.5–4 mg kg⁻¹. The results showed that use of polar (CN and NH₂) and non-polar (C₁₈ and phenyl) adsorbents resulted in acceptable recoveries (41–95%). C₁₈–MSPD co-column lanthanum silicate was preferred, because it gave the best recovery and cleanest extract. The polarity of the eluting solvent relative to that of the solid support bonded phase plays a significant role in determining what remains on the column and what is eluted. Four eluents for the MSPD column were examined. The results, shown in Table II,

Table II

Average recoveries (*R*, %) and relative standard deviations (*RSD*, *n* = 3) obtained by use of different eluents

Pesticide	CH ₃ OH		CH ₂ Cl ₂		CH ₂ Cl ₂ -Ethyl acetate (1:1)		Ethyl acetate	
	<i>R</i> (%)	<i>RSD</i> (%)	<i>R</i> (%)	<i>RSD</i> (%)	<i>R</i> (%)	<i>RSD</i> (%)	<i>R</i> (%)	<i>RSD</i> (%)
Diazinon	26	9	56	11	94	13	53	10
Ethion	32	8	64	9	95	7	44	15

indicate that dichloromethane–ethyl acetate, 1:1, resulted in the best recoveries of diazinon and ethion. Detection limits, obtained by direct injection of the standard mixtures and calculated for a signal-to-noise ratio

of three [10], were 0.02 mg kg⁻¹ for ethion and 0.035 mg kg⁻¹ for diazinon. Maximum residue limits (MRL) for diazinon and ethion permitted by the Codex Alimentarius Commission [11] on samples similar to pistachio nuts (0.1 mg kg⁻¹) are higher than the detection limits obtained in this work. Thus, this method is effective for extraction of diazinon and ethion in pistachio nuts.

Optimization of Thin-Layer Chromatography

For rapid identification of diazinon and ethion residues in the MSPD extract, the chromatographic behavior of the organophosphorus pesticides on the lanthanum silicate and lanthanum tungstate ion exchangers was studied with several mobile phases. When lanthanum silicate ion exchanger was used for TLC CH₃OH–10% NH₃, 9.5:0.5, was found to be the most suitable mobile phase for clear separation of diazinon and ethion from the pistachio extract. When the lanthanum tungstate ion exchanger was used as TLC adsorbent CH₃OH–CH₂Cl₂–10%NH₃, 6.5:3.1:0.4, was found to be the most effective mobile phase. The *R_F* values obtained are listed in Table III.

Table III

The *R_F* values obtained

Ion-exchanger	Diazinon	Ethion
Lanthanum silicate	0.79	0.69
Lanthanum tungstate	0.98	0.90

CONCLUSION

A simple and rapid method has been developed for simultaneous determination of diazinon and ethion in pistachio nuts. It combines the advantages of rapid ion-exchange TLC detection with those associated with MSPD – rapid analysis and avoidance of expensive and toxic solvents. It is suitable for the analysis of organophosphorus residues at levels down to the MRL in pistachio nuts, using only 0.5 g sample.

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