

# Evaluation of Efficient Extraction Method for the Determination of Carbaryl Residue in Olive Oil

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## Abstract

Carbaryl was analyzed in olive oil using solid phase extraction (SPE) with lanthanum silicate as a new solid sorbent followed by high performance liquid chromatography with UV-VIS detection (HPLC-UV). The various parameters influencing extraction such as different eluents, volumes of eluent, conditioning pH and several spiked concentrations were studied to determine the optimum conditions for lanthanum silicate- SPE. Mean recovery with methanol as eluent was 76% with RSD 2-3% in concentration range of 0.5-32 ppm. The limit of detection (LOD= 1.03 mg kg<sup>-1</sup>) was lower than maximum residue limit (MRL) established by WHO/FAO.

**Keywords:** Carbaryl; HPLC; Lanthanum Silicate; Olive Oil

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## 1. Introduction

Carbamate pesticides have become increasingly important in recent years, due to their broad spectrum of activity, relatively rapid disappearance, but since they are inhibitors of acetylcholinesterase, they are considered toxic for the environment and for human beings [1,2]. Detection of their residues in food has aroused a great deal of public concern because carbamates are used in households and in agriculture on a large number of crops. Analysis involves a number of stages such as extraction, removal of interfering substances from the extract and determination [3-5]. The development of small, disposable cartridge systems containing solid adsorbents, has greatly speeded up the extraction process prior to analysis. However new selective adsorbents are needed to expand the area of application of this technique. During the last two decades, new synthetic inorganic ion exchangers have been developed

which show high selectivity toward certain elements [6-8] and may be used as potential sorbents in SPE applications. Lanthanum silicate, a promising ion exchanger [9] shows unusual selectivity [10,11] has been employed here to develop a SPE method for carbaryl residue in olive oil.

## 2. Methodology

### 2.1 Chemicals and materials

Carbaryl standard was from supelco and other chemicals were of analytical grade or HPLC grade (E. Merck or Aldrich). Stock solution was prepared in methanol with a pesticide concentration of 1000 mg lit<sup>-1</sup> and was 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.

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## 2.2 Apparatus

A waters HPLC with UV-VIS detector, waters 20-port vacuum manifold apparatus and pH meter (Horriba, M-12) were used.

## 2.3 Preparation of Lanthanum silicate

Lanthanum silicate was prepared [9] by mixing the lanthanum chloride (0.1 M) and sodium silicate (0.1 M) solutions in the volume ratio (1:3). On standing overnight the white gel formed is settled. It was filtered off, washed three times with nonopure water and dried in oven at 50°C. The dried gel was finally ground and sieved.

## 2.4 Extraction Procedure

The olive oil samples for analysis were obtained from a local market and spiked with carbaryl to give pesticide concentrations of 0.5, 1, 10, 16 and 32 mg kg<sup>-1</sup>. Samples were then allowed to stand at room temperature for 1 h and diluted with hexane in the volume ratio of 1:9. Solid phase extraction was prepared with a 6 ml syringe barrel column with polyethylene frits. The syringe barrel column was packed with 500 mg lanthanum silicate sorbent. SPE columns were used in conjunction with a standard vacuum manifold apparatus. The column was conditioned with 1 ml methanol and the diluted sample solution containing carbaryl residue was passed through the column. Interferences were washed with 3 ml hexane. Methanol (1.5 ml) was used as the final eluent. The SPE-extract was collected into a graduated conical tube (15 ml) and

evaporated to dryness under stream of nitrogen gas. The resulting material was dissolved in methanol (1 ml) and analyzed by HPLC with UV-VIS detection.

## 2.5 Chromatographic Conditions

The sample extracts were analyzed using a waters HPLC system equipped with a waters 600E solvent delivery unit, a millford 2487 dual wavelength UV-VIS detector ( $\lambda = 280\text{nm}$ , sensitivity = 2 AUFS), a Rheodyne 772 si injection valve with a 20 ml sample loop and spherisorb-C<sub>8</sub> column (250× 46 mm, 5  $\mu\text{m}$ ). The mobile phase was a mixture of methanol and water in a volume ratio of 70:30 and the flow rate was set at 1 ml min<sup>-1</sup>

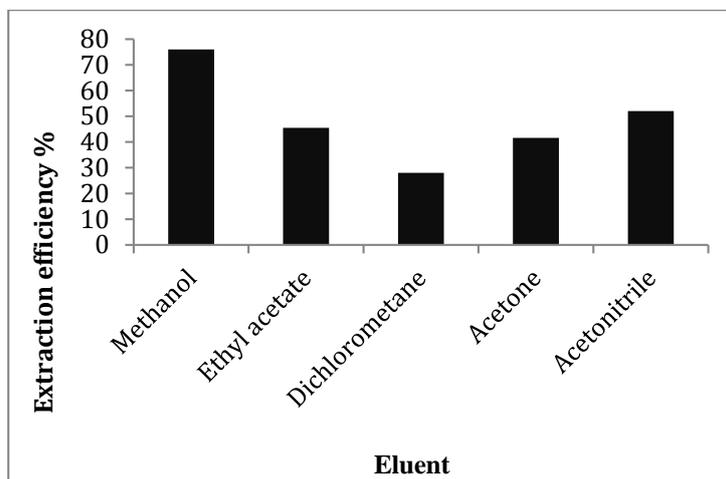
## 3. Results and Discussion

### Optimization of the Solid Phase Extraction

The optimization of extraction involved the study of the following parameters: different eluents, volumes of eluent, conditioning pH and several spiked concentrations. The goal of this optimization was to obtain the highest absolute recovery of carbaryl.

### 3.1 Eluent Selection

Different eluents such as methanol, Acetonitril, Ethyl acetate, acetone and dichloromethane were tested following the procedure reported in section extraction procedure. Figure. 1 shows the variation of efficiencies at different eluents. Since methanol gave better results it was chosen for further studies.

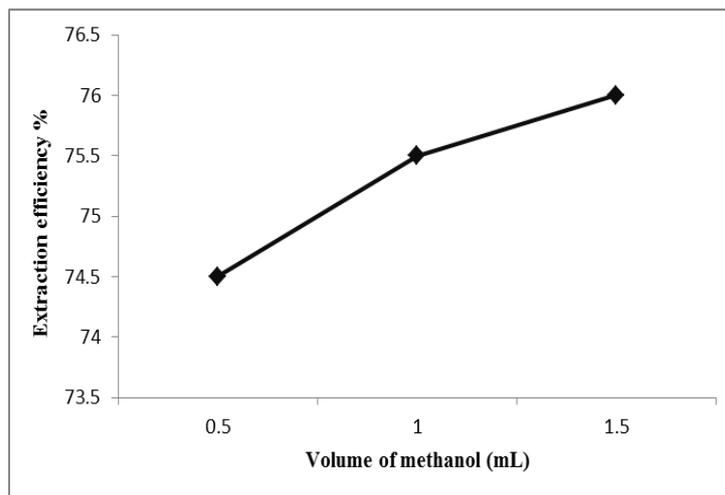


**Figure 1.** Effect of type of the eluent on the extraction efficiency. Concentration of carbaryl: 16 mg kg<sup>-1</sup> (n=3).

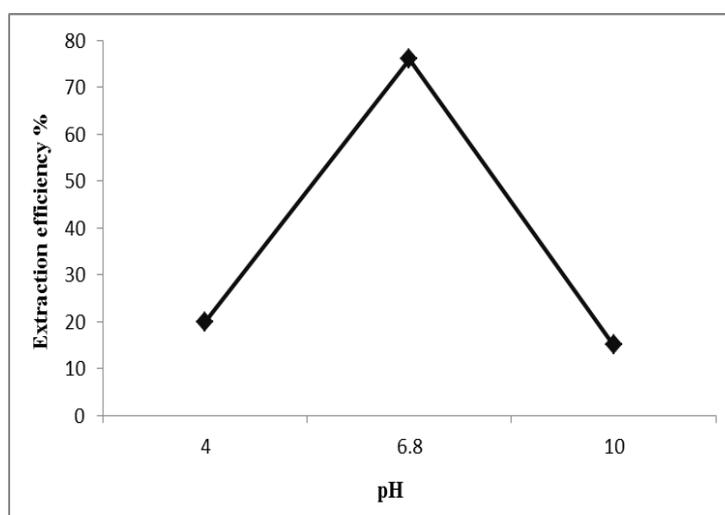
### 3.2 Eluent Volume

After choosing methanol as appropriate eluent, it is necessary to optimize its volume. In order to study

this effect, the methanol volume varied between 0.5 and 1.5 mL. The results showed that (Figure 2) eluent volume had no significant effect on extraction efficiency.



**Figure 2.** Effect of volume of methanol on the extraction efficiency. Concentration of carbaryl: 16 mg kg<sup>-1</sup> (n=3).



**Figure 3.** Effect of pH on the extraction efficiency. Concentration of carbaryl: 16 mg kg<sup>-1</sup> (n=3)

### 3.3 Effect of pH

The effect of pH on the conditioning step was investigated using 1 ml buffer (NH<sub>3</sub>/NH<sub>4</sub>Cl 1M and CH<sub>3</sub>COOH/CH<sub>3</sub>COONa 1M) with pH 4, 6.8 and 10. In addition to buffer, the column was conditioned with 1 ml methanol. As can be seen in figure 3, the best recovery was obtained at the pH 6.8.

### 3.4 Effect of Initial Concentrations

Olive oil was spiked with carbaryl at the range of 0.5, 1, 10, 16 and 32 mg kg<sup>-1</sup> and lanthanum silicate SPE procedure was done as mentioned in section extraction procedure. The results are shown in figure 4. It can be seen that the extraction efficiency increased with the increasing of initial concentrations up to 16 mg kg<sup>-1</sup> of carbaryl and remained almost constant at higher concentration.

### 3.5 Figures of Merit

Calibration curve of carbaryl was constructed after extraction of a standard series of spiked olive oil samples with a determination coefficient of 0.999. Limit of detection (LOD) was obtained by progressively diluted standard solution to the peak height of carbaryl was 3 of the background noise [12]. LOD based on S/N = 3 was 1.03 mg kg<sup>-1</sup> and was lower than maximum residue limit (MRL) of carbaryl in olive oil (25 mg kg<sup>-1</sup>). Relative standard deviations (RSD) were 2-3% (n=3).

## 4. Conclusions

The obtained results demonstrate that lanthanum silicate SPE affords a simple, convenient and rapid methodology for preconcentration of carbaryl residue in olive oil. Based on the achieved consequences, the presented procedure is suitable

for the analysis of carbaryl residue at level down to MRL.

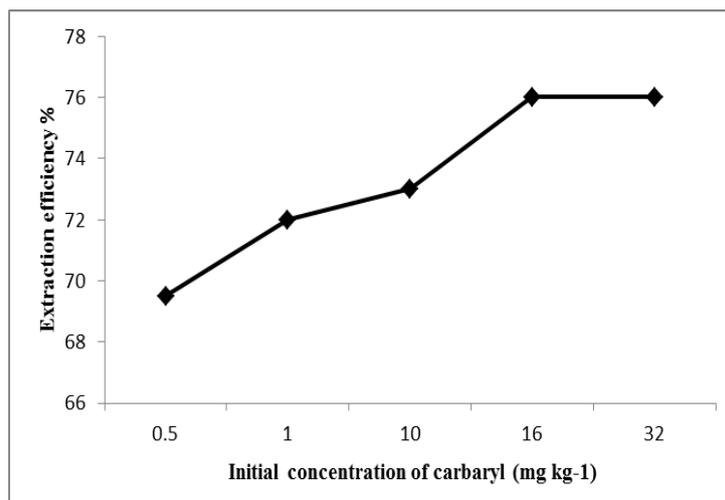


Figure 4. Effect of initial concentration of carbaryl on the extraction efficiency.

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