

SAMPLE HANDLING. CHROMATOGRAPHIC ANALYSIS OF TRIFLURALIN FROM ENVIRONMENTAL SAMPLE. I. WATER SAMPLE

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ABSTRACT. Trifluralin is a preemergent herbicide with little postemergent activity. When incorporated in the soil it is effective for the control of annual grasses and broad-leaved weeds in beans, soyabeans, sugar beet, sunflower, and tomatoes. That is why trifluralin can be found in small quantities in the soil and accidentally, in greater concentrations in soil and water as a consequence of other human activities in the field.

In the analytical chain, sample handling is very important for the accuracy and the precision of the analysis. This pesticide is extracted from environmental water sample using liquid-liquid extraction and solid phase extraction.

The present paper deals with SPE of trifluralin on C18 cartridge. The efficiency of the sample treatment was evaluated by the recovery degree of the pesticide from spiked water samples.

When methanol was used as a conditioning and elution solvent, the recovery was higher than 90% and the reproductibility was better.

INTRODUCTION

2,6- dinitro-N,N-dipropyl-4-trifluoromethylaniline or trifluralin (fig 1.) is an orange crystalline solid, melting point 48,5 – 49°C, small solubility in water 1mg/mL, maximum solubility in xilen 580g/mL.

Trifluralin

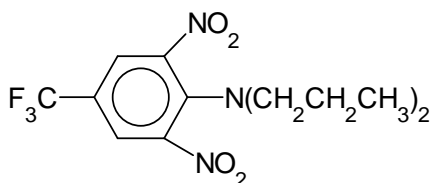


Figure 1. Trifluralin structure.

In a study [1] for the determination of trifluralin from water, Colina used the solid phase extraction on C18 cartridge. The sorbent conditioning was achieved with 5 mL isooctane, ethyl acetate, methanol and water passed successively through the cartridge. After analyt retention achieved at a flow rate 10-15 mL/min. the sorbent was washed with water and dried with air. The elution was achieved with a solvent mixture consisting in ethyl acetate – isooctane (1:1, v/v). The elution solvent evaporated and the residuum was dissolved in 1 mL methanol. This procedure provides a 96% recovery. The same procedure applied on river water provides a 85% recovery.

Senseman [2] used Empore C18 discs in order to concentrate trifluralin from water. When the ethyl acetate was used as elution solvent, the recovery was 72,3%.

Triska [3] used a mixture of dichlormethan-acetone (1:1, v/v) as eluent. Generally, in order to isolate the trifluralin from water, C18-sorbent and ethyl acetate or ethyl ether [4] as elution solvent were used, the recovery being 65%-96%.

Because of the high volatility of these solvents and because they are not mixable with water, in this paper we try to use methanol either as conditioning and elution solvent. As the solid phase for the extraction three different sorbents synthesized by three different procedures were used.

As analytical procedure in order to determine trifluralin gas chromatography was used. [5 - 7]. In this study we have analyzed trifluralin also using liquid-chromatography.

CHEMICALS AND STANDARD SOLUTION

Solvents from Chimopar (Bucuresti, Romania), trifluralin – technical grade from CIG –Turda (Romania), solid phase cartridge SepPack C18, Merck (Darmstadt, Germany) were used and a methanol solution containing 10,85 µg trifluralin / mL for gas-chromatography and another one containing 100µg trifluralin / mL for liquid chromatography analysis were prepared.

PROCEDURE

I. Water Sample Analysis by Liquid-Chromatography

a) Sample preparation using SPE

The extraction cartridge containing 300 mg sorbent was prepared. The characteristics of this sorbent are presented in Table 1.

Table 1.

The characteristics of the three different sorbents used in the SPE procedure

Sorbent	Sil C18 (I)	Sil C18(II)	Sil C18(III)
SiOH residual (%)	28,73	22,06	8,91
pH	3,9	4,5	4,8
Hydrophobic parameter - % methyl red remain in the solution	62,19	68,998	73,53
Carbon content (%)	7,63	11,4	7,57
IR analysis (Absorbivity at 2950cm ⁻¹)	0,0714	0,0766	0,0235
Thermogravimetric analysis (weight losses – mg)	7,4	12	8
Ligand density (µmol/g)	1,581	2,56	---

The sorbent conditioning was achieved in two ways:

- 5 mL methanol
- 5 mL acetone followed by 5 mL methanol.

The solvent excess was removed with 5-mL water. The trifluralin retention from the synthetic sample (100mL water spiked with 1 mL stock solution - 100µg trifluralin / mL) was achieved by passing it through the cartridge at a flow rate 10 mL/min. The cartridge was then washed with 5-mL water, air- dried and the analyt eluted in two ways:

a) 3 mL methanol

b) 3 mL acetone.

The organic solvent evaporated and the solid residuum was dissolved into 1 mL methanol. The symbols for this sample are given in Table 2.

b). Chromatographic analysis

The determination was achieved on a Hewlett Packard 1100 liquid-chromatograph, with manual injection (20 μ m microcolumn), operated at 25°C. A Lichrosphere RP 60 Select B, 250mmx4mm column was used. The mobile phase was an acetonitrile – water (85:15, v/v) mixture, at a 1 mL/min flow rate. The detection was achieved in UV at 275nm, where the trifluralin has a maximum absorbance spectrum (fig.2)

Table 2.

The symbol for each sample obtained after the SPE procedure

Sorbent	Conditioning and elution type	Nr. of extraction	Symbol
Sil C 18 I	A	1 ; 2 ; 3	Ia ₁ ; Ia ₂ ; Ia ₃
	B	1 ; 2 ; 3	Ib ₁ ; Ib ₂ ; Ib ₃
Sil C 18 II	A	1 ; 2 ; 3	IIa ₁ ; IIa ₂ ; IIa ₃
	B	1 ; 2 ; 3	IIb ₁ ; IIb ₂ ; IIb ₃
Sil C 18 III	A	1 ; 2 ; 3	IIIa ₁ ; IIIa ₂ ; IIIa ₃
	B	1 ; 2 ; 3	IIIb ₁ ; IIIb ₂ ; IIIb ₃
Sil C18 IV (Sep Pack C18)	A	1 ; 2 ; 3	IVa ₁ ; IVa ₂ ; IVa ₃
	B	1 ; 2 ; 3	IVb ₁ ; IVb ₂ ; IVb ₃

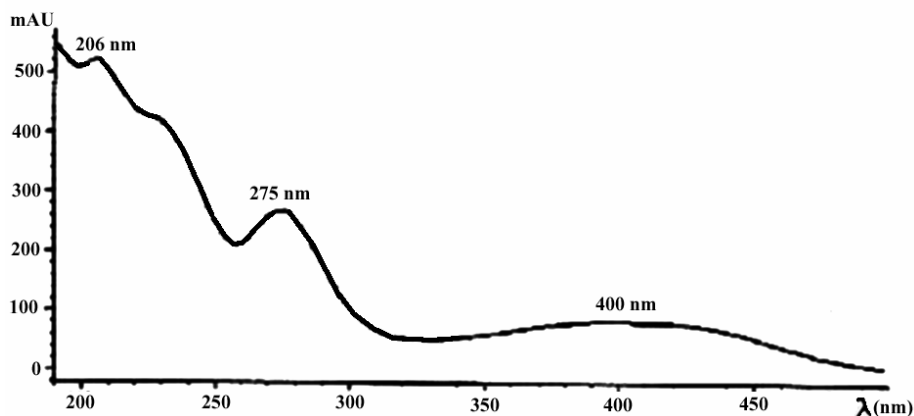


Figure 2. Absorbance spectrum.

RESULTS AND DISCUSSION

In Figures 3 and 4 the bi- and tri-dimensional chromatograms for trifluralin in stock solution are presented. The chromatographic peak of trifluralin was observed at 3.89 min retention time. The recovery was calculated by dividing the peak area of trifluralin from the processed sample by the peak area of trifluralin from the stock solution. Table 3 presents the recoveries after the SPE procedures presented above.

Table 3.

The recoveries of trifluralin when using different sorbents and elution solvents.

Sample	Recovery (GR%)			Average GR% \pm RSD%
	Extr.1	Extr.2	Extr.3	
Ia	52,51	54,75	53,29	53,52 \pm 2,124
Ib	45,50	43,25	44,45	44,4 \pm 2,536
IIa	52,62	48,43	48,26	49,77 \pm 5,00
IIb	49,92	43,52	45,92	46,45 \pm 6,96
IIIa	60,80	54,60	58,54	57,98 \pm 1,961
IIIb	51,66	54,74	53,49	53,30 \pm 2,908
IVa	54,77	57,55	56,39	56,24 \pm 2,489
IVb	41,96	45,93	40,88	42,92 \pm 6,198

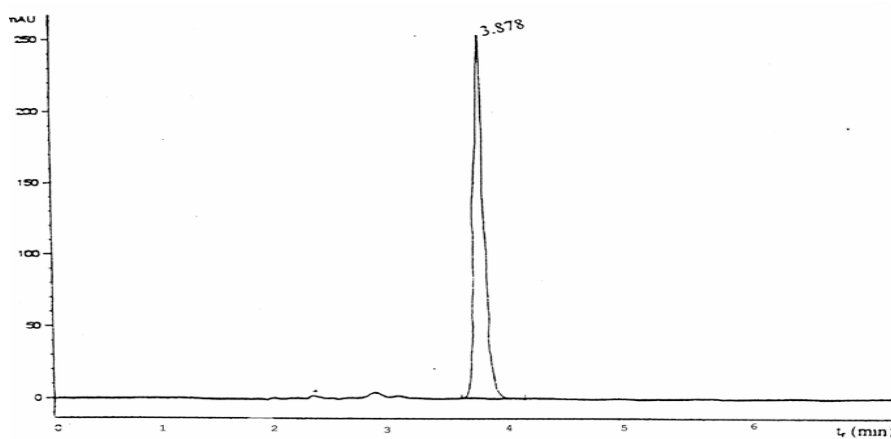
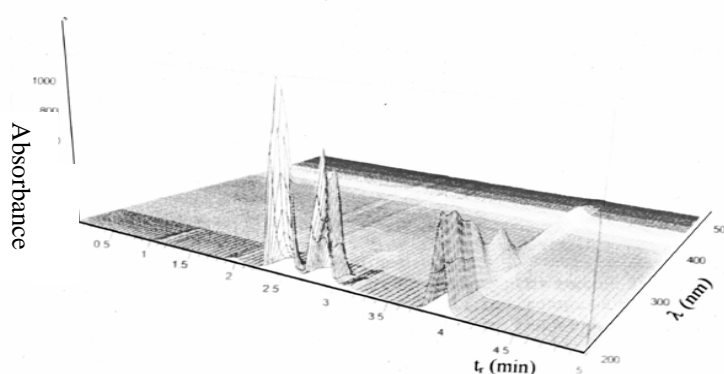
Figure 3. The trifluralin chromatogram ($\lambda = 275$).

Figure 4. The tridimensional chromatogram for trifluralin.

In Figure 5 there is the recovery as the chart of the sorbent and elution solvent type.

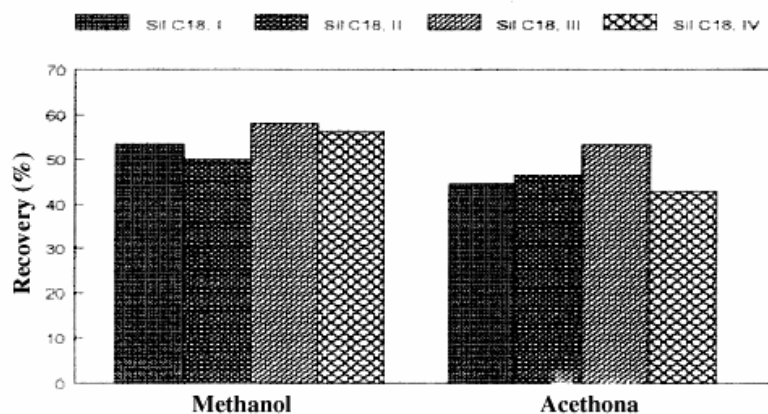


Figure 5. The sorbent and the eluent influence on the recovery.

The small recovery values can be explained only by analyt losses in the evaporation phase, when variable quantities of trifluralin also evaporated.

II. Water Sample Analysis by Gas-Chromatography

a). Sample preparation using SPE

After cartridge preparation the sorbent was conditioned in two ways:

- 5 ml methanol
- 5 ml ethyl acetate followed by 5 mL methanol.

The conditioning solvent was then removed with 5 mL water. The trifluralin retention from the synthetic sample (100 mL water spiked with 1 mL stock solution 10,85µg/mL) was achieved at a 10 mL/min flow rate. After the sorbent was dried, trifluralin was eluted in two ways:

- 1 mL methanol
- 1 mL ethyl acetate.

The volume of the sample was then adjusted to 1 mL with methanol, respectively with ethyl acetate.

b) Chromatographic analysis

The determination was achieved on a Fractovap 2450, Karlo Erba gas chromatograph equipped with capture electron detector. The stainless steel column filed with OV 17 (methylphenil silicon), 3% on a Gas-Chrom support, was operated at 170°C. As eluent was used nitrogen at 15mL/min flow rate.

Results and discussions

In these condition the peak of trifluraline was observe at 7.4 min. retention time. In Table 4 are given the recoveries calculated in the same manner like presented before.

In Figure 6 there is the recovery as the chart of the sorbent and elution solvent type.

Table 4.

The recoveries of trifluralin when using different sorbents and elution solvents.

Sorbent	Recovery (%)						Average GR±RSD (%)
	Solvent						
	Ethyl Acetate	Methanol					
		Extra. 1	Extra. 2	Extra. 3	Extra. 4	Extra. 5	
Sil C18 I	107,5	98,35	103,75	107,25	81,75	81,00	94,42±12,33
Sil C18 II	83,14	107,25	99,38	99,14	78,87	80,62	93,05±12,59
Sil C18 III	87,43	99,00	105,00	102,00	86,25	80,25	94,50±10,7
Sil C18 IV	92,57	95,14	96,75	94,50	99,75	96,00	96,43±2,04

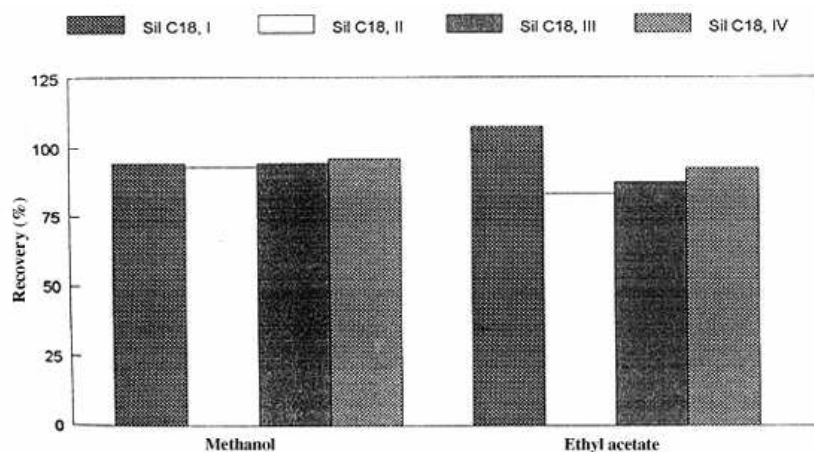


Figure 6. The sorbent and the eluent influence on the recovery

In this experiment, it can be observe that the recovery values are higher as first attempt. These can be explained by avoiding the evaporation phase. So, the recovery increased from 50% at 90%.

CONCLUSIONS

It is clear that the preparation step is very important in obtaining accurate results. So, when evaporation step is eliminated the recovery increased from 50% to 90%. Better reproductibility were achieved when a polar organic solvent, like methanol, mixable with water was used.

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