

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, soybeans, 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 solid phase extraction (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 reproducibility was better.

Keyword: trifluraline, SPE, GC, HPLC, water.

I. Introduction

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

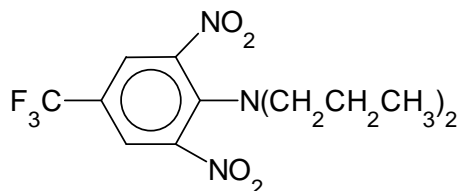


Figure 1. Trifluralin structure.

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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 or solid phase extraction.

The present paper deals with solid phase extraction (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.

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 perform with a solvent mixture consisting in ethyl acetate – isooctane (1:1, v/v). The elution solvent was 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. When Empore C18 discs and ethyl acetate as elution solvent were used the recovery for trifluralin from water samples was 72,3% [2]. Other solvents like ethyl ether [3] or a dichlormethan-acetone (1:1, v/v) mixture [4] were also used, the recovery ranging between 65%-96%.

In last period sample preparation for trifluralin involved solid phase microextraction (SPME), a new technique that do not need solvents [5].

Generally gas chromatography is used for trifluralin identification and quantification [6-8].

II. Experimental

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.

For the extraction of trifluralin three types of home made Sil C18 was used. The chemicaly modified surface was achived using three different procedure, obtaining three sorbent with different properties (Sil C18 I, Sil C18 II, Sil C18 III) [9]. It was also used a comercial SepPack C18 cartridge from Merck.

Also we try to use liquid-chromatography instead of gas 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

Sample preparation using SPE

1. Water Sample Preparation for Liquid-Chromatography

The extraction cartridge containing 300 mg sorbent was prepared. The sorbent conditioning was achieved in two ways:

- a) 5 mL methanol
- b) 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 was evaporated and the solid residuum was dissolved into 1 mL methanol. The symbols for this sample are given in Table 1.

Table 1.

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

2. Water Sample Preparation for Gas-Chromatography

After cartridge preparation the sorbent was conditioned in two ways:

- a) 5 ml methanol
- b) 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:

- a) 1 mL methanol
- b) 1 mL ethyl acetate.

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

Chromatographic analysis

1. HPLC 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).

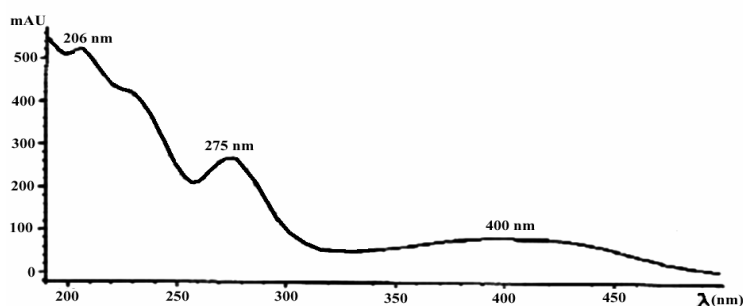


Figure 2. Absorbance spectrum.

2. Gas-Chromatography Analysis

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

III. Results and discussion

1. Water Sample Analysis by Liquid-Chromatography

In Figure 3 the chromatogram for trifluralin in stock solution is 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 2 presents the recoveries after the SPE procedures presented above.

The small recovery values can be explained only by analyt losses in the evaporation phase, when variable quantities of trifluralin also evaporated. A slightly increasing of recovery was observed in case of methanol elution.

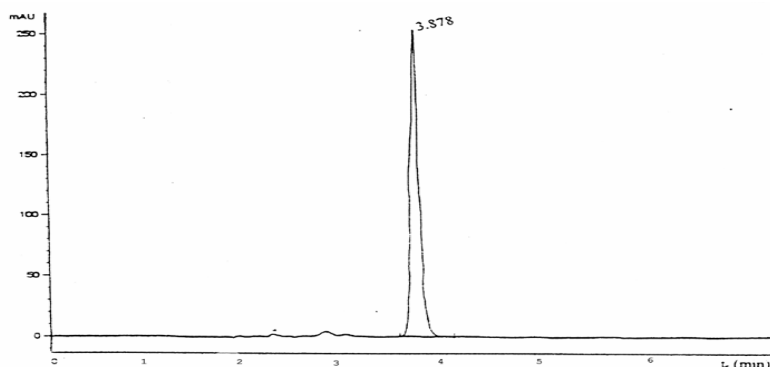


Figure 3. The trifluralin chromatogram ($\lambda = 275$).

Table 2.

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

2. Water Sample Analysis by Gas-Chromatography

In these condition the peak of trifluraline was observe at 7.4 min. retention time. In Table 3 are given the recoveries calculated in the same manner like presented before.

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

Table 3.

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

Sorbent	Recovery (%)						Average GR±RSD (%)
	Solvent						
	Ethyl Acetate	Methanol					
		Era. 1	E 2	Ext 3	Ex. 4	E. 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

IV. 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%. For different C18 phases, better reproductibility were achieved when a polar organic solvent, like methanol, mixable with water was used.

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