

## METHOD FOR THE DETERMINATION OF TRICLOPYR RESIDUES IN SOIL

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### Abstract

In this study, a method for the determination of triclopyr in soil samples has been developed. The analyte was extracted with acidified acetonitrile, while the determination and quantification of triclopyr were performed by high-performance liquid chromatography (HPLC) with a diode array detection. Optimal HPLC-DAD conditions were: mobile phase acetonitrile and 0.1% H<sub>3</sub>PO<sub>4</sub> (50:50), the flow rate of 0.9 ml/min, and 220 nm of wavelength. In terms of method validation, accuracy (expressed as recovery), linearity, precision (RSD) and LOQ were determined. Obtained results for the recovery using this method, at the three spiking levels, were 81-93%. Precision, expressed as RSD, was 9.1%, while the LOQ was 0.01 mg/kg. Therefore, it can be concluded that the proposed method could be applied for the analysis of triclopyr residues in the soil samples.

### Introduction

Triclopyr (3,5, 6-trichloro-2-pyridyloxyacetic acid) [1] is an auxin-type, post-emergent herbicide, widely used for weed control in pastures, rangelands and non-crop areas (Figure 1). After application, it is rapidly absorbed by the foliage and roots and translocated throughout the plant, inducing an auxin-type response in susceptible plant species, causing epinastic bending and twisting of the stems that result in growth inhibition [2, 3]. Triclopyr has shown high efficacy for a wide variety of annual and perennial broadleaf weeds.

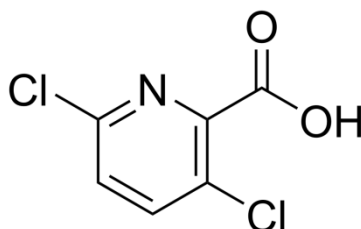


Figure 1. Triclopyr – structural formula

However, with their widespread use in agriculture, the potential adverse effects of their residues becoming evident. Due to their intensive use, herbicides fate and their presence in the environment become a great concern.

Due to agricultural activities, residual activity in the soil can result in damage to succeeding crops, contamination of water sources by leaching, and toxicity to non-target organism. Triclopyr concentrations remain in the soil after application, are of great concern. Residual herbicide may affect the growth of succeeding vegetation and can reach groundwater. The trace determination of herbicide residues, generally in environmental samples, presents a challenging analytical problem [4].

In order to evaluate the presence of triclopyr residues in the soil, it is necessary to apply the appropriate method. Aim of this study was to develop and validate the method for the determination of triclopyr residues in soil.

## Experimental

Analytical standard of triclopyr (purity 95%) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Acetonitrile (HPLC grade) and phosphoric acid were provided by J.T. Baker (Deventer, The Netherlands), while water was purified by Milli-Q (Millipore, Billerica, MA, USA) system. For the extraction, QuEChERS sorbent kits and pouches of salts were purchased from the Agilent Technologies (Cat. No. 5982-5650).

For the method validation blank soil samples were used. Previously, soil samples were homogenized, sieved (2 mm) and air-dried at room temperature before their use.

Triclopyr was extracted from soil by modified QuEChERS method. Ten grams of homogenized soil sample in a 50 mL polypropylene tube was enriched with the appropriate amount of triclopyr analytical standard. Afterward, 10 mL of acetonitrile was added and hand-shaken for 1 min. A mixture of buffered salts (4 g  $\text{MgSO}_4$ , 1 g NaCl, 1 g trisodium citrate dihydrate and 0.5 g disodium hydrogen citrate sesquehydrate) was added, hand-shaken for 1 min, vortexed for 1 min, centrifugation at 3000 rpm during 5 minutes.

A separated acetonitrile layer was filtered through a 0.45  $\mu\text{m}$  nylon filter to an autosampler vial and analyzed using HPLC/DAD.

Validation of the method was performed through the following parameters: linearity, accuracy, precision, and limit of quantification (LOQ).

## Results and discussion

For the chromatographic analysis, an Agilent 1100 Series system with DAD detector and Zorbax Eclipse XDB-C18 (50 mm  $\times$  4.6 mm, 1.8  $\mu\text{m}$ ) were used. The mobile phases, composed of acetonitrile and 0.1% phosphoric acid (50/50, V/V) were pumped at a flow rate of 0.9 ml/min, while wavelength was 220 nm (Figure 2 and 3).

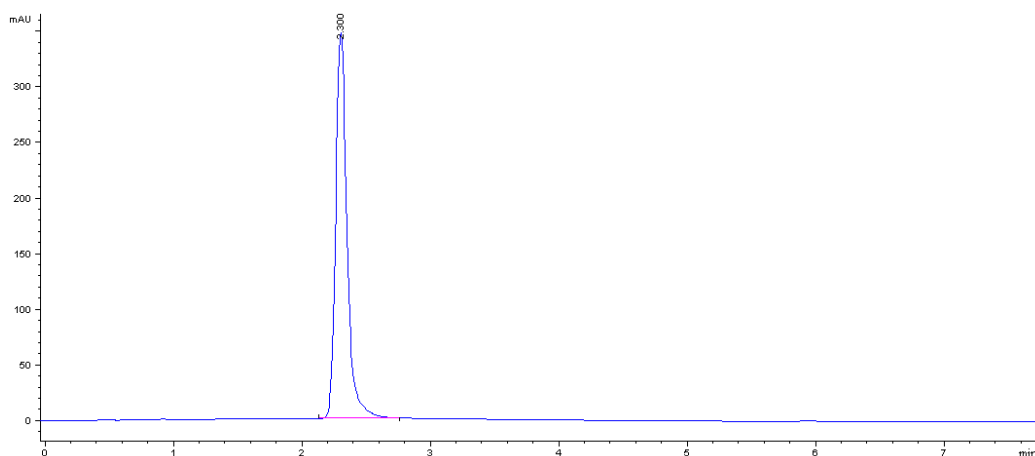


Figure 2. HPLC/DAD chromatogram of triclopyr in acetonitrile

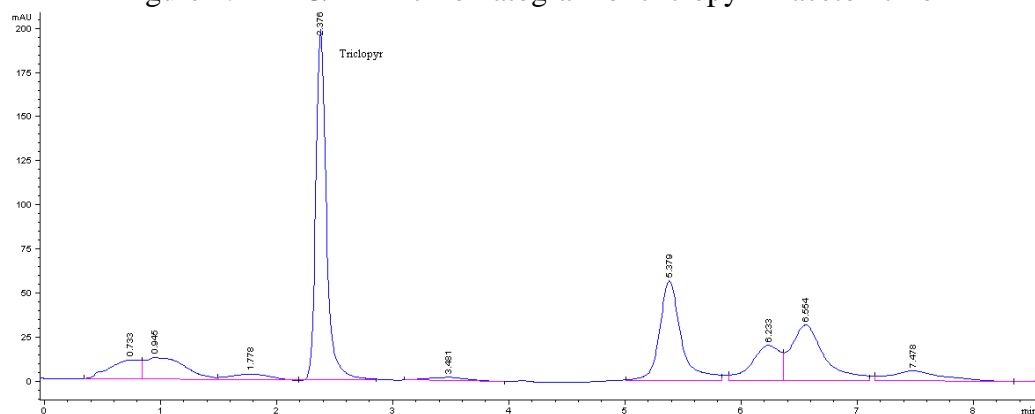


Figure 3. HPLC/DAD chromatogram of triclopyr in soil matrix

Method for the determination of pesticide residues in soil samples has been validated in accordance with SANCO/3029/99 rev.4 11/07/00 [5]. The achieved values completely fulfilled the required criteria (Table 1).

Table 2. Analytical parameters for HPLC/DAD determination of triclopyr

Parameter	Concentration interval ( $\mu\text{g/ml}$ )	Slope <sup>a</sup>	Correlation coefficient <sup>a</sup>	Recovery (%)	LOQ (mg/kg)
Triclopyr	0.01-120	3.29	0.999	81-93	0.01

$$^aY = ax + b$$

The QuEChERS method, without purification step, was applied to estimate the effectiveness of the method. Obtained results for the recovery using this method, at the three spiking levels, was 81-93%. Precision, expressed as relative standard deviation, was 9.1%, while the limit of quantification was 0.01 mg/kg.

All of these parameters meet the SANCO criteria that prescribe yield extraction of 70-110%, precision reported as repeatability less than 20%, and quantification limit of at least 0.05 mg/kg.

### Conclusions

In this study, methods based on reversed-phase liquid chromatography and modified QuEChERS method was validated. The proposed procedure, without cleanup, is more practical due to the consumption of less solvent in comparison with the method including purification step. According to SANCO criteria, results of all analyzed parameters were satisfied, recommending this method for use on real soil samples.

### Acknowledgement

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