ANALYSIS EMERGING CONTAMINANTS IN THE WATERS WASTE AND DRINKING

Cozma Alina*, **Bota Sanda***, **Cărăban Alina***, **Toderaş Monica***,
Filip Sanda*, **Macocean Eugen*** , **Toderaş Alexandru****

* University of Oradea, Faculty of Sciences, University St. No.1. Oradea, 410087, Romania
e-mail: acozma@uoradea.ro
** Liceul Teoretic C-tin Șerban, Aleșd

Abstract

The paper was aimed to analyze contaminants class of herbicides present in wastewater and drinking water respectively. The analysis was performed by high performance liquid chromatography. After analyzing drinking water was established the existence of contaminants in samples bentazone, 2,4,5-T, Mecotrop, compounds from the class of herbicides fenoxiclorurate.

Key words: contaminated herbicides fenoxiclorurate, SPE, HPLC

INTRODUCTION

Occurrence of trace organic contaminants from wastewater, the behavior during wastewater treatment and drinking water production are key issues in the re-use of water resources. It was found that different classes of contaminants (such as those resulting from the degradation of the surfactants, pharmaceuticals and pesticides polar) derived from the treatment of waste water can be found in low amounts, such that one of the sources of such contaminants and metabolites their sewage waters. (Sawyer, 1993, Shalaby, 1990).

In some studies it has found that antibiotics are most marked since emerging contaminants in the environment emanating lead to the emergence of resistant bacteria. However, there are other emerging contaminants, especially those polar acidic products such as antibiotics, pesticides, acid and acidic metabolites of surfactants, which deserves special attention. This category due to physico - chemical properties (high water solubility, low degradability) are able to penetrate all filtration systems, presenting a potential risk to drinking water. (Grou et al., 1979, Rodil et al., 2012,)

An important class of herbicides often used is the fenoxiacizii and their derivatives. They are characterized by a high polarity and thermal instability. Fenoxiacizii is used both in agriculture and households. These compounds to be detected at trace levels to ensure appropriate quality of drinking water and food, and to verify removal of these pollutants from contaminated resources.

This group of herbicides include: 2,4-diclofenoxiacid acid (2,4-D), 2-(2,4-dichlorophenoxy) propionic acid (dicloprop), dicamba, 2,4,5 acid - triclorofenoxiacetic (2,4, 5 - T), 4- (2,4-diclofenoxi) butyric acid (2,4 - DB) of 4 - chloro-o-toliloxiacetic (MCPA), etc.

Along with other emerging contaminants, pesticides polar elimination rate were quite low and have been detected in surface waters. Analysis of these contaminants is quite difficult due to variation in their chemical properties, but mostly because of low concentrations (usually ppb or even ppt) find themselves in their matrix and complexity. (Hura, 1995, Steinheimer et al., 2001, Communal, Royer, 2004,)

The presence fenoxiclorurat acid herbicides (commonly used worldwide) in the waters of the environment is well documented, but their behavior during wastewater treatment has been studied less. Currently, the methods used to determine phenoxy acid herbicides, chlorinated technique are dominated by gas - chromatographic detect either EDC or MS. The main disadvantage of gas analysis - Chromatography is that first requires a derivatization step, typically using diazomethane - a highly toxic and carcinogenic - or, more rarely, acid anhydride or alkylchloroformate. It has been proposed as an alternative technique LC-MS. In this case, the phenoxy acid herbicides - chlorinated detected in the negative ionization conditions, freeing - is typical ion [M-H] - and a moiety found in abundance formed by loss of acidity. (Liteanu, 1989, Liteanu et al., 1974, Gocan, 2002, Savici, 1980)

MATERIAL AND METHOD

It looked at a mixture containing the following herbicides: 2,4 dichlorophenoxyacetic, 2,4,5 -trichlorophenoxyacetic, bentazone, dicamba, mecoprop and 4-chloro - o - toliloxiacetic (MCPA). In the first stage it was carried out in solid phase extraction (SPE) followed by analysis by high performance liquid chromatography (HPLC).

The conditions of extraction are as follows: they worked with a Lichrolut type extraction column RP-18 (500 mg - 3 mL) as solvent A - methanol B - water, C water adjusted to pH 3 with 85% phosphoric acid. Conditioning of the column extraction was performed using 3 ml of each solvent. Was injected 1 liter sample of conditioned water in the extraction column by means of an extraction device which is connected to the sample through a capillary tube of PTFE and steel. The injection was done in the column under vacuum for 4 hours. Zephon hose was passed through an adapter which is connected to the column. To prevent disconnection adapter spine was fixed with a clamp. Washing was performed with 1 mL water. Drying of the tubing was made with dry nitrogen for 60 minutes at a steam pressure of 2-3 bar. The sample was eluted once with 1.5 mL methanol, and then the solvent was evaporated and the residue was dissolved in one mL of mobile phase.

The chromatographic analysis by high performance liquid chromatography was performed using a separation column type LiChrospher 60RP SelectB, 5µm, 250x4,6mm column protection LiChrospher 60RP SelectB, 5 mm, 4x4mm. It worked with two mobile phases: A - acetonitrile + 100 ml 96% acetic acid and B - KH2PO4 (5 mmol / L) + 100 µLacid 96% acetic acid. Detection was conducted under UV light at 228nm, column temperature 350C, injection volume of 100 ml and the elution at a flow rate of 1mL / min.

RESULTS AND DISCUSSION

To establish the optimal working conditions and measure parameters of the separation was prepared and analyzed standard solution containing a known quantity of possible contaminants from the water main. Standard solution was prepared by dissolving the following compounds dicamba, bentazone, 2,4-D, MCPA, 2,4,5-T dichlorprop, mecoprop in water to give 300 ng / l.

The chromatogram obtained by the analysis of this solution is shown in Figure No. 1

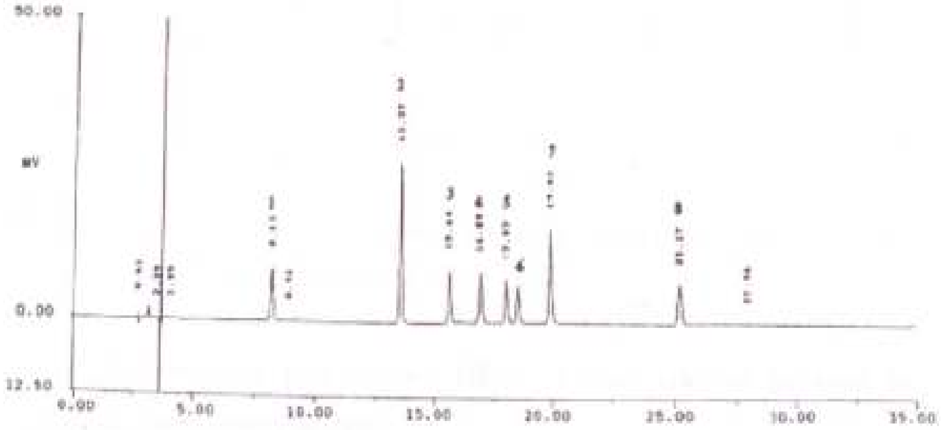

Fig.1 – Chromatogram No. 1 - standard calibration solution

Following the optimization of separation conditions were established the following conditions

- Mobile Phases: A - acetonitrile + 100 ml acetic acid 96%
  B - KH2PO4 (5 mmol / L) + 100μL 96% acetic acid.
- Elution rate of 1 mL / min.
- Column temperature 350C
- Detection was conducted under UV light at 228nm,

More determinations were made by calculating the degree of recovery of components taking into account the concentration of the standard. In Table. 1 shows the results and the retention time of each contaminant in the water. Prepared by the method were obtained degree of 95-104% recovery of the acid compounds fenoxiclorurat, which proves that the optimum parameters are established analysis.

Table 1

Recovery levels (average values) based on the retention times

Name	Degree of Recovery	Time (RT)
Dicamba	100%	8,1 min
Bentazon	104%	13,5min
2,4 – D	95%	15,6min
MCPA	95%	16,8min
2,4,5 – T	97%	17,9min
Diclorprop	99%	18,4min
Mecoprop	103%	19,8min

Method for determining a herbicide contaminants fenoxiclorurat acid was used for the analysis of drinking water. For these determinations 1 liter of water concentrated by the method in solid phase extraction (SPE) procedure and then the methanolic solution obtained was analyzed by the chromatographic method developed.

The chromatograms obtained are:

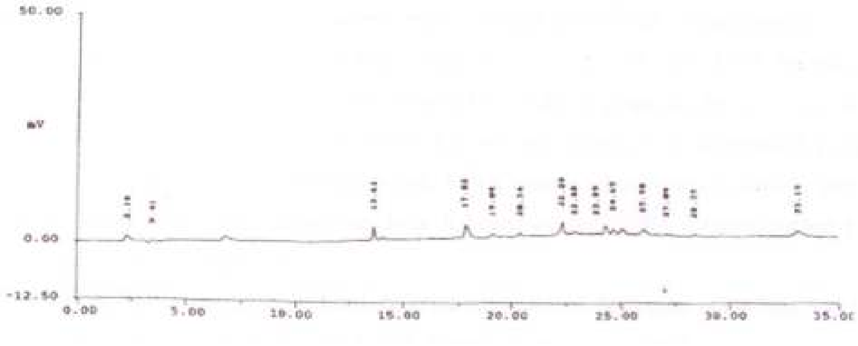

Fig. 2 - Chromatogram No.2 - after SPE sample of tap water

Analyzing the results it is observed that there are small amounts of contaminants in drinking water. In order to identify the peaks corresponding to each contaminant was enriched sample to be analyzed with an amount of the standard solution corresponding to 30 ng / bit. The chromatogram obtained is shown in Fig. 3

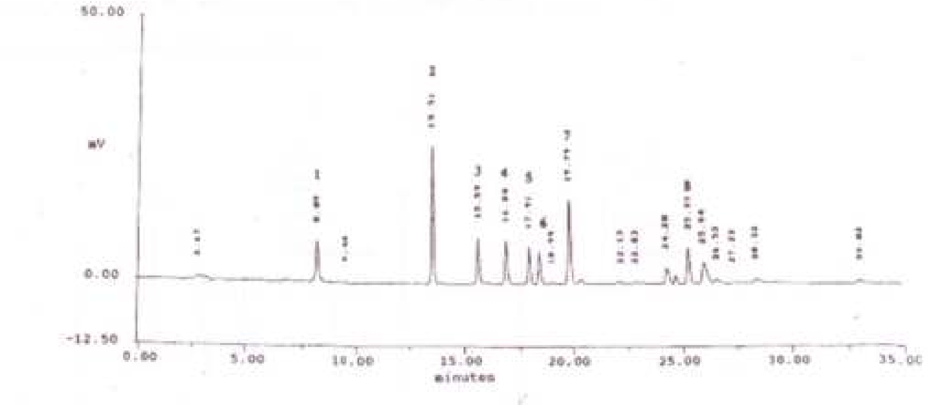

Fig. 3 - Chromatogram No. 3 - sample (1 liter of tap water) enriched with an amount of 300ng / L per component (30 ng / little, if recovery is 100%)

The analysis results are found in drinking water contaminants determined existence: bentazone (Rt = 13.4 min), 2,4,5-T (Rt = 17.9), Mecotrop (Rt = 19.04).

CONCLUSIONS

This paper presents the results obtained from experiments for the determination of contaminated acid compounds fenoxiclorurat. Analyzing a standard solution containing compounds dicamba, bentazone, 2,4-D, MCPA, 2,4,5-T, dichlorprop, mecoprop in a concentration of 300 ng / l each, were established the optimal separation conditions, by calculating the the recovery and retention time of each component.

Using the method developed was analyzed a sample of drinking water. One liter of sample was concentrated using solid phase extraction method, and the extract was subjected to chromatographic determination. It was determined the existence of three contaminants of this class of compounds bentazone (Rt = 13.4 min), 2,4,5-T (Rt = 17.9), Mecotrop (Rt = 19.04).

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