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Determination off-line and on-line of methidathion trace in drinking water

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Abstract

In this study, a fast, simple and sensitive analytical method was developed for the determination of methidathion, organophosphorus pesticide, in water. The methidathion is determined at μg L^{-1} level in different types of drinking water, making a preconcentration with a C-18 silica column and analysis by HPLC with a UV-Vis detector. The preconcentration is performed in off-line (using C-18 silica extraction cartridges) and on-line (using precolumns). With both methods of preconcentration, we can reach methidathion in determining the concentrations of the order of μg L^{-1} or ηg L^{-1} when the amount of adsorbent is increased in the cartridges. In off-line method several important solid phase extraction SPE parameters were optimized, extraction efficiency as a function of sample volume and elution mixture. Methidathion were eluted form cartridges with 5 mL of MeOH:H_2O (80:20, v/v) and 1500 mL of sample could be percolated. Under the optimum extraction conditions, this method showed low limit of quantification (0.1 mg L^{-1}), but the low recovery (50-12%) of the methidathion in environmental samples may appreciate the limitations of the method off-line to analyze traces of methidathion in aqueous samples. On-line extraction presented that the use of precolumns allows faster determination without risk of contamination with a smaller sample volume and improved coefficient of variation (<7.8%), achieving recoveries of 100% and detection limit 0.4 μg L^{-1}.

Keywords: drinking water, methidathion, SPE.

1. Introduction

The use of pesticides for the control of crop pests and weeds, plus the discharges from manufacturing plants, accidental spills, and natural processes such as dilution, surface runoff and leaching, are the causes of the occurrence of these xenobiotic compounds in surface waters. That is the reason why the control of pesticides in surface, drinking and groundwater is nowadays a real necessity[1,2]. In recent years, organophosphorus pesticides (OPPs) have been the largest type of pesticides used worldwide. However, OPPs are known as the most poisonous class of pesticides[3]. It causes the inhibition of acetyl-cholinesterase in the central nervous systems[4-6]. Therefore, it is crucial to monitor the trace levels of OPPs in environment particularly such as drinking water. One problem associated with the application of organophosphorus is the need to monitor their levels in the environment, especially in water, in view of their ability to accumulate[7]. The monitoring of pesticides in water samples has been an intense field of research in the past 10–20 years. The analysis of pesticides in water samples is a problem of primary concern for quality control laboratories due to the toxicity level of these compounds and their public health risk[8]. Analytical methods are needed to measure pesticides in water to determine their fate and transport in the environment. Currently, there are hundreds of pesticides registered for use in the United States[9]. In Mexico, water intended for human consumption must meet minimum specified requirements, including for pesticides a maximum level for each pesticide of 0.03 µg L^{-1} in some case, and a maximum of 50 µg L^{-1} for pesticides such as 2,4 -D and methoxychlor[10]. The analysis of water samples for the presence of pesticides is fraught with difficulties, since preparation of samples is an arduous, time-consuming process, which can itself give rise to additional contamination and errors. The generally low levels of target analyses and often the complexity of the matrix are further problems with which the analyst has to contend. Regarding the new legislation, the information concerning the monitoring of pesticides and the technical specifications for their measurement in water samples where ultra-sensitive analytical methods are required[11,12]. For some compounds, like pesticides, there is still a need to improve the performance of the existing methods. High sensitive techniques like gas chromatography tandem mass spectrometry (GC–MS/MS) and liquid chromatography coupled with mass spectrometry (LC–MS) have been developed. However, for most of the substances present at trace and ultra-trace levels the extraction and pre-concentration steps are so far essential for their detection. In Mexico the use of organophosphate pesticides is widely distributed, as in the case of methidathion, an organophosphate pesticide, Methidathion[13-15]. [O,O-dimethyl-S-(5-methoxy-1,3,4-thiadiazolinyl-3-methyl) dithiophosphate] is an organophosphate chemical employed commercially as an agricultural pesticide since 1966[16]. It was chosen as the target molecule for the present study because of its biotoxicity. Oral LD_{50} values of methidathion in animals are 52 mg kg^{-1} in mice, 48 mg kg^{-1} (male) and 40 mg kg^{-1} (female) in rats[2], or 31 mg kg^{-1} (male) and 32 mg kg^{-1} (female) in rats[3]. The solubility of this compound in water is greater than the average solubility of many other organophosphorus compounds (240 mg L^{-1}) and its relative stability to hydrolysis; they together have a strong possibility of contaminating the water[14]. Hence the importance of generating rapid and continuous information on water quality to minimize the risks associated with the use of these pollutants. The analytical determination of this compound in complex samples such as natural and/or drinking water is reported in several references[3,7,17-19]. The main difficulty of trace-level analysis is that it can only be analyzed when a preconcentration of the sample is carried out with proper disposal of interfering agents. To perform its control in the environment and food should develop methods of highly selective and sensitive analysis. Since the concentrations of the OPPS are in trace amounts, pre-concentration techniques are required to determine these compounds in the real samples.

The most common and conventional technique for the analysis of OPPs in water is the Solid-phase extraction (SPE), this is an efficient method for the concentration and cleanup of organic contaminants in water. Several types of cartridges have been used in prior studies (e.g., C-8, C-18); they are capable of extracting multiple pesticide classes. The principles are based on the distribution of solutes between a solid phase and the aqueous sample is a viable option for preconcentration of very diluted aqueous samples. The SPE is a variation in the extraction procedure based on the distribution, adsorption, ion exchange or affinity[20,21]. This technique has been widely accepted because it is faster than many conventional techniques and moreover it is suitable for highly polar contaminants (log P <1), intermediate (log P 1-3) and low (log P>3), depending on the adsorbent used[22]. The SPE can be considered as a simple process of liquid chromatography, wherein the adsorbent is the stationary phase and the mobile phase is water in the aqueous sample during the extraction step or the organic solvent during the elution step. Organic compounds that are not eluted with water are trapped on the adsorbent. The SPE can be performed off-line, i.e., as a separate step of chromatographic analysis or real-time or on-line, when directly coupled to chromatographic analysis. Removing interfering compounds the detection can be accomplished in a relatively simple manner with the use of mixtures having different polarities of elution and extraction capabilities. Additionally, on-line methods have several advantages over other extraction methods, such as speed, the use of small sample volumes, easy automation and eliminating contamination risks, because there is no sample manipulation between the preconcentration stage and analysis[23,24]. The purpose of this work is to develop an analytical procedure that can determine the methidathion in drinking water at concentrations of the order of mgL^{-1} or ngL^{-1} comparing two methods of preconcentration by SPE, coupled line (on-line) and a deferred (off-line) analyzing by HPLC.

2. Materials and Methods

The methidathion standard was of Analytical Pesticide grade with certified purity of 99.0% and was purchased from Chem Service (West Chester, USA). Concentrated pesticide solution with a concentration of approximately 100 mg L^{-1} were prepared in methanol and kept at 4±2 °C, protected from light. Working standard solutions were always freshly prepared by dilution of the methidathion standard solution in water with approximately 0.5% of methanol, in order to obtain a final concentration of about 1 µg L^{-1}. The aqueous samples were filtrated with a nylon membrane of 47 mm and pore size of 0.45 µm, coupled to a Sartorius filtration system. Organic solvents (Methanol, acetonitrile, water) were pesticide or HPLC grade and were purchased from EM Science NJ. USA. M. Perchloric acid (>99.0%) and sodium hydroxide (analytical grade) were obtained from Sigma-Aldrich (USA).

2.1. Instruments

A 785 HPLC system (Perkin-Elmer) connected to a 785 A UV/vis spectrometer (Perkin-Elmer), equipped with a binary pump model 776 and was used to perform the HPLC analysis. A Nucleosil C-18 (150 mm x 4.6 mm i.d.), (Supelco) chromatographic column was used for pesticide separation. For the on-line method, the aqueous samples were concentrated in a PRP-1 (25 mm x 4.5 mm i.d., 5 µm) stainless steel pre-column, (Phenomenex, USA). The on-line system was built in a series of capillary stainless steel tubes attached to two valves Rheodyne Cotai, model 7000 with six inputs and two-way. And an isocratic pump ELDEX, CC-100-S model, with a stainless steel pre-column preconcentration. The off-line extraction step was carried out using a vacuum box (Supelco) of 10 positions with gentle vacuum (4-way Isco, WIZ model). C-18 Sep-Pak cartridges (500 mg) (Waters, Milford, MA, USA) were used for off-line SPE optimization.

2.2. Chromatographic analysis

The composition of the mobile phase was determined conducting the retention curves at different percentage of organic solvent (acetonitrile or methanol) in water, it was tested in a range of 85 -55% organic solvent.The flow rate was 1 mL min^{-1} and the injection volume was defined by the 20-µL Rheodyne loop.

2.3. Quantitation

The Calibration curve was constructed for methidathion by injecting eight calibration standards directly into the HPLC, at the concentrations 50, 45, 40, 25, 15, 10, 5 and 1 mg L^{-1}. Calibration curves were constructed each time a new sample set was analyzed in order to accurately compensate for the day-to-day variation of the control standards.

2.4. Sample preparation (SPE)

The preconcentration of the aqueous samples were made in cartridges (methodology off-line) and guard column (methodology on-line) and the results were compared with each other. The optimization of the conditions of deferred preconcentration was based on the study of extraction efficiency as a function of sample volume and elution mixture, implemented through extraction in cartridge of different volumes of HPLC grade water and drinking water distribution network added with the constant amount of methidathion.

2.5. Selecting the elution phase

SPE was carried out using *C-18 Sep-Pak* cartridges of 500 mg. To evaluate the SPE performance a control standard was submitted to the extraction procedure. The SPE was performed by analyzing spiked water samples at the concentration level of 3 mg L^{-1} of methidathion, 250 mL of sample were percolated in each assay. Various elution mixtures were tested to determine their composition and optimal recovery volume. Several mobile phases tested to elute the pesticide form cartridges were the following:

- First fraction: 5mL MeOH:H_2O (v/v): 100:0; 85:15; 80:20; 70:30; 60:40; 50:50.
- Second fraction: 5mL with the same composition in order to be sure that all analyte was recovered.
- Third fraction: Finally, 5mL of methanol was percolated in order to be sure that all analyte was recovered.

A 20 µL aliquot of each extract was analyzed by HPLC to calculate the percentage of recovery from methidathion from extraction cartridge.

2.6. Recovery Performance

The extraction yield curve based on the volume of break leak was determined. Fortified samples of ultrapure water and drinking water spiked with a constant amount of methidathion, 0.15 mg was percolated. Volumes were tested: 250, 500, 1000, 1250, 1500 mL at a constant flow of 3 mL min^{-1}.

2.7. Preconcentration on-line

On-line methodology involves placing a precolumn in place of injection loop into the six-valve ports and with two positions. After conditioning the adsorbent, sample application and perform an eventual cleaning using a pump in the position of "charge", the precolumn is coupled to an analytical column connecting the valve in position "inject". Then the retained compounds are eluted directly from the guard column to the analytical column with the mobile phase which allows the separation. Device is showed in Figure 1.

3. Results and Discussion

Selection of the mobile phase: In the two organic solvents (acetonitrile and methanol) tested, methanol was chosen, even though both the two solvents were appropriate to carry out adequate retention and separation methidathion from other peaks. The mobile phase of 50 to 60% MeOH has an adequate retention time to conduct proper analysis and separation of methidathion and spikes that might occur at the void volume. Linearity and detection limit: The value of the correlation

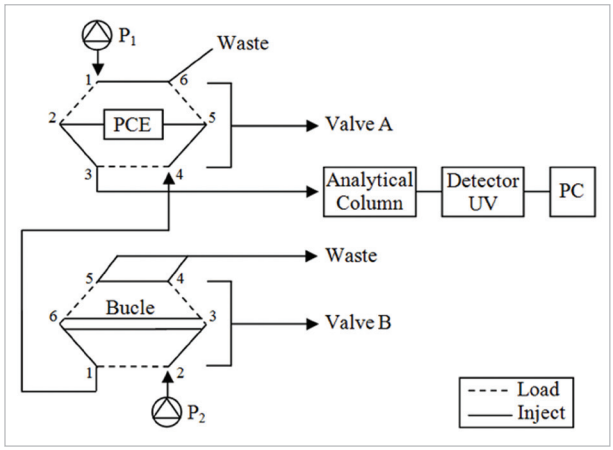

Figure 1. Experimental setup for the preconcentration, extraction and on-line analysis (PCE = precolumn, UV = ultraviolet, PC = personal computer).

coefficient (r) obtained was 0.9951, a= 41887, b= 32398 which means it has a very close positive correlation to 1. The detection limit was considered as the concentration that causes a peak height corresponding to 3 times background noise, which was determined by injecting increasingly dilute methidathion solutions. The obtained concentration was 5 mg L^{-1} using a 20 µl loop, with a detection limit of 100 ηg absolute injected.

3.1. Preconcentration in off-line

The methodology off-line is established as follows: The C-18 SPE cartridges were preconditioned by eluting with 5 mL of HPLC grade MeOH, followed by 30 mL of HPLC grade water, being careful not to dry the stationary phase. Then, the samples were percolated a flow of 2.5 mL min^{-1} using a vacuum box, immediately the stationary phase was washed with 5 mL of HPLC grade water and dried for 10 min. After, the moderately polar interfering compounds were eluted with 5 mL of MeOH:H_2O (50:50, v/v). This elution mixture only desorbed from the stationary phase to moderately polar compounds, without eluting methidathion. Then moderately polar compounds as methidathion were eluted with 5 mL of MeOH:H_2O (80:20, v/v). Finally, non-polar compounds were eluted with 5 mL of MeOH, and also it was check if everything methidathion was eluted with the previous mixture. Actually, we verified that all methidathion was eluted in the previous mixture. The extracts were evaporated to dryness, and reconstituted with 0.5 mL of MeOH. Samples were then analyzed by HPLC. In addition, 5 mL of spiked MeOH:H_2O (80:20, v/v) at concentration level of 3 mg L^{-1} methidathion was evaporated and reconstituted to determine losses by evaporation. The residue was re-dissolved with 0.5 mL methanol and analyzed by HPLC. Residue peak area obtained practically corresponds to a concentration of 30 mg L^{-1}, thus there was not loss by evaporation of the analyte, this is because the methidathion acted as a moderately volatile compound.

The breakthrough volume was determined by testing different volumes of HPLC water sample spiked at 0.15 mg -250, 500, 750, 1000, 1250 and 1500 mL- and correlating the volumes with the corresponding chromatographic peak areas. The results presented in Table 1 show that the recovery ranged from 82 to 101, without showing a correlation between sample volume and % recovery. Pesticide recovery can be considered independent from sample volume up to 1500 mL of sample, showing a slight variation when volume of sample increased. However, recovery methidathion from the drinking water samples ranged from 50.5 to 12.0 %, in general it had lower recoveries. The results presented in Table 2 show that the breakthrough volume reached a volume lower than 250 mL with a recovery of only 50% of methidathion, for high sample volumes the recovery is lower, only 12%. It is more noticeable that in the sample with dilute concentrations (0.1 mg L^{-1}) very low recoveries

Table 1. Recoveries % HPLC grade water sample of methidathion as a function of sample loading volume through a cartridge (500 mg C18).

Percolated volume (mL)	Concentration (mg L^{-1})	Recovery (%)
250	0.60	101
500	0.30	89
750	0.20	98
1000	0.15	82
1250	0.12	89
1500	0.10	102

Constant amount of methidathion spiked: 0.15 mg.

Table 2. Recoveries % in drinking water sample of methidathion as a function of sample loading volume through a cartridge (500 mg C-18).

Percolated volume (mL)	Concentration (µg/L)	Recovery (%)
250	0.60	50.50
500	0.30	43.00
1000	0.15	50.00
1500	0.1	12.00

Constant amount of methidathion spiked: 0.15 mg.

were observed. Moreover, the chromatographic analysis of the extract of the elution mixture comprises of methanol (third fraction) not containing methidathion, so we conclude that methidathion was not retained completely on the stationary phase cartridge. It means that matrix effects may have an excessive influence on the recovery. In spite of the studies being carried out on samples of drinking water, it is known the bad quality of water due to the presence of ferrous compounds as well as organic matter for this reason we consider this factor influenced the poor retention of methidathion in the stationary phase C-18. Even after percolating the sample we observed one soiling in the cartridges. It is known that DOC may bind to analytes carrying them through the SPE cartridge, thereby not allowing them to attach to the stationary phase. In addition, DOC may saturate the active sites of the sorbent, which will also affect relative recoveries. Finally, large humic molecules may hinder the penetration of the elution solvent to the sorbent bound analytes[24]. These factors usually result in decreased recoveries, the same in our case.

Figures 2 shows HPLC chromatograms of HPLC grade water and drinking water sample spiked at the 0.6 mg L^{-1} level and preconcentred in cartridge. The low recovery of the compound in environmental samples may appreciate the limitations of the method off-line to analyze traces of methidathion in aqueous samples, among them the largest sample handling requiring an evaporation and reconstitution of the concentrate, causing a risk of contamination and losses, moreover reducing sensitivity to inject only an aliquot of the extract.

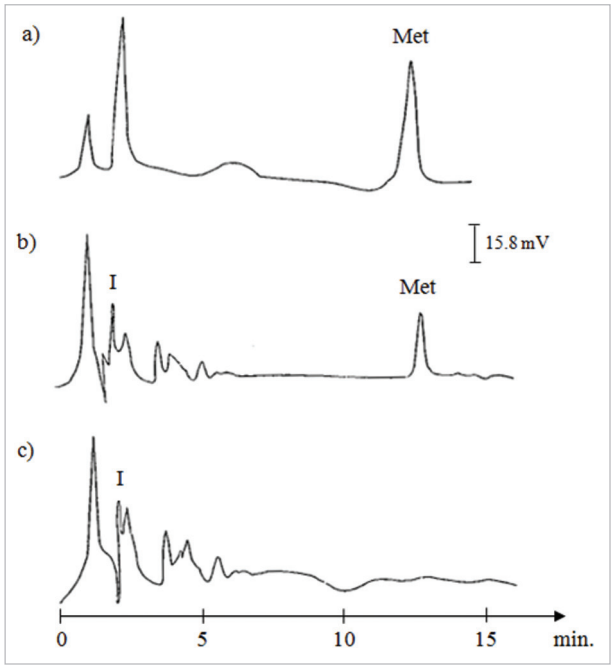

Figure 2. Chromatograms obtained from a SPE of 250 ml water at concentration of 0.6 mg L^{-1} Methidathion, a) drinking water b) HPLC grade water c) drinking water without spiking. Met= methidathion, I= interfering compounds.

3.2. Preconcentration on-line

3.2.1. Selection of the mobile phase elution

The methodology on-line is described below:

The extraction precolumn was preconditioned by eluting with 25 ml of HPLC grade water at flow 1.5 mL min^{-1}, using the auxiliary pump, the analytical column is conditioned while. Then the sample is percolated at same flow. Once loaded solutes wash the interstices of the guard and the connections with 3 mL of HPLC grade water, immediately the solutes were eluted on-line with the same mobile phase MeOH:H_2O (65:35, v/v) of chromatography analysis. A standard solution was analyzed to determine the percent recovery.

3.2.2. Study of the breakthrough volumes

The breakthrough volume was determined by testing different volumes of a 0.8 µg spiked tap water sample-50, 70, 100, 150, 250 mL-and correlating the volumes with the corresponding chromatographic peak areas. The results presented in Table 3 show that the

Table 3. Recoveries % in drinking water sample of methidathion as a function of sample loading volume through a C-18 Nucleosil, 5 µm, 1.3 cm x 4.6 mm d.i. precolumn.

HPLC grade water			Drinking water		
Percolated volume (mL)	Concentration (µg/L)	Recovery (%)	Percolated volume (mL)	Concentration (µg/L)	Recovery (%)
50	16.00	100.00			
70	11.42	101.00	70	11.42	103.00
100	8.88	90.00	100	8.00	98.00
150	5.30	110.00	150	5.33	99.00
170	4.70	101.00			
250	3.20	100.00			

Spiked water samples with 0.8 µg methidathion.

Table 4. Precision, expressed as relative standard deviation for four replicates. 100 mL sample.

Sample	Concentration (µg/L)	Recovery (%)	RSD
Drinking water	8.88	98	7.37
HPLC grade water	8.88	90	8.97

Spiked water samples with 0.8 µg methidathion.

breakthrough volume was not reached by any of the compounds until 250 mL since the recovery of about 100% was obtained. Pesticide recoveries from both water samples were mainly between 98–110%. The procedure was independent on sample concentration over the range 16-3.2 µg L^{-1}. Due to practical reasons, we selected 100 mL, which enabled the necessary concentration factor to achieve acceptable detection limits.

This procedure was applied to drinking water and HPLC grade water samples, spiked at the 8.8 µg L^{-1} level. Table 4 shows the recoveries for methidathion and the precision, expressed as relative standard deviation, for four replicates. Each sample was analyzed independently by the same analyst and equipment, obtaining a repeatability or precision (measured as relative standard deviation (RSD) of 7.37 and 8.97 % respectively. The repeatability was typically higher, with a value less than 10% of RSD.

Figure 3 shows the chromatograms from the analysis of three samples of drinking water spiked at 1 µg

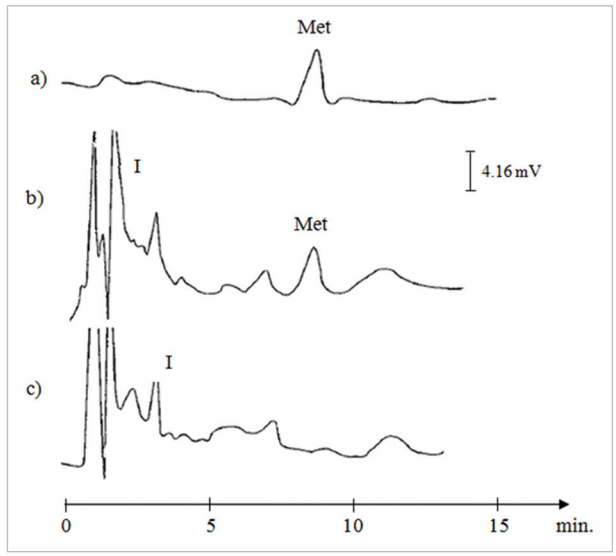

Figure 3. Chromatograms obtained from a SPE of 100 ml water at concentration of 1 µg L^{-1} Methidation, a) HPLC grade water, b) drinking water spiking c) drinking water without spiking. Met= methidathion, I= interfering compounds. "Nucleosil". Precoluma extraction.

L^{-1} of methidathion, 100 ml of sample were percolated through the precolumn, samples without spiking no peak was found. The spiked samples show that the peak of the compound is clearly visible and it could be assumed that further diluted samples could be analyzed. For example if the sample volume was 250 ml could be obtained such a peak at a concentration of 0.4 µg L^{-1}. The methods used in this study were tested and optimized for factors that can affect extraction efficiencies. For water samples, volume of the sample, and concentration of pesticide, along with the appropriate solid phase and elution solvents are all

important factors that can affect extraction efficiencies. The methods developed for this study were designed to be simple and thus useable in most laboratories. As it can be seen, this procedure allows the determination of the above mentioned pesticide in a drinking water sample with good recoveries and precision and avoids the need of duplicated water samples for the separated extraction

4. Conclusions

With both methods it was possible to determine the concentrations at which the order methidathion μg L^{-1} and ηg L^{-1} be reached if the amount of adsorbent is increased, in the case of extraction in off-line. Both methods can quantify the presence of methidathion if it is in aqueous samples at concentrations of the order of μg L^{-1}.

The on-line extraction method also has the advantage of avoiding the risk of contaminating samples because there is no contact between the sample preconcentration step and analysis, producing better recoveries and precision.

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References

[1] Beitz, H., Bewick, D. W., Guyot, C. N., Häfner, M., Herzel, F., James, M. O., Schmidt, H. 2012. Pesticides in ground and surface water Vol. 9. H. Börner (Ed.). Springer Science & Business Media.

[2] Vieira, D. C., Noldin, J. A., Deschamps, F. C., Resgalla Jr., C. 2016. Chemosphere 162:48-54.

[3] T. Takayasu, Y. Ishida, M. Nosaka, M. Kawaguchi, Y. Kuninaka, A. Kimura, T. Kondo. 2012. Legal Medicine 14:263–266.

[4] Pundir, C. S., & Chauhan, N. 2012. Analytical Biochemistry, 429:1: 19-31.

[5] Coskun, R., Gundogan, K., Sezgin, G. C., Topaloglu, U. S., Hebbar, G., Guven, M., & Sungur, M. 2015. Nigerian journal of Clinical Practice, 18:5:644-650.

[6] Hulse, E. J., Davies, J. O., Simpson, A. J., Sciuto, A. M., & Eddleston, M. 2014. American Journal of Respiratory and Critical Care Medicine, 190:12:1342-1354.

[7] Ibrahim, W. A. W., Veloo, K. V., & Sanagi, M. M. 2012. Journal of Chromatography A, 1229:55-62.

[8] Rodrigues, A. M., Ferreira, V., Cardoso, V. V., Ferreira, E., & Benoliel, M. J. 2007. Journal of Chromatography A, 1150:1:267-278.

[9] Hladik, M. L., Smalling, K. L., & Kuivila, K. M. 2008. Bulletin of Environmental Contamination and Toxicology, 80:2:139-144.

[10] Norma Oficial Mexicana NOM-127-SSA1-1994, Salud ambiental. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización

[11] TenBrook PL, Tjeerdema RS, Hann P, Karkoski J. 2009. Rev Environ Contam Toxicol. 199:19-109.

[12] Vanatta, L. E., & Coleman, D. E. 2007. Journal of Chromatography A, 1158:1:47-60.

[13] Hijar M, Monroy A., Rascon A. 1996.Toxicology Letters, 88:1:52-53.

[14] CICLOPLAFEST. 1994. Catálogo oficial de plaguicidas. SARH. México, D.F.

[15] Hernandez-Romero, A. H., Tovilla-Hernandez, C., Malo E. A., Bello-Mendoza, R. 2004. Marine Pollution Bulletin 48:1130–1141.

[16] Baselt RC. 2008. Disposition of toxic drugs and chemicals in man. 8th ed. Foster City, CA: Biomedical Publications. 963–4, 1657–9.

[17] Arques, A., Amat, A. M., Santos-Juanes, L., Vercher, R. F., Marin, M. L., & Miranda, M. A. 2009. Catalysis Today, 144:1:106-111.

[18] Sanchez, L., Romero, E., Castillo, A., & Pena, A. 2006. Chemosphere, 63:4:616-625.

[19] Sanagi, M. M., Abidin, N. A. Z., Heng, S. H., & Ibrahim, W. A. W. 2008. Malaysian Journal of Analytical Sciences, 12:3: 570-574.

[20] S.K. Zervou, C. Christophoridis, T. Kaloudis, T. M. Triantis, A. Hiskia. 2016. Journal of Hazardous Materials. xxx xxx–xxx.

[21] Pailler, J. Y., Krein, A., Pfister, L., Hoffmann, L., & Guignard, C. 2009. Science of the Total Environment, 407:16:4736-4743.

[22] Guene M., Hennion M.C.. 1994. J. Chromatography A, 665:243-251.

[23] Goewie C.E. Kwakman P., Frei R.W., Brinkman U.A. 1984. J. Chromatography, 284:73-86.

[24] Smyth M.R. 1992. Chemical analysis in complex matrices. Ellis Howood and PTR. Prentice Hall. 59-69. London, Uk.