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Development and validation of method for the determination of organochlorine pesticides and trihalomethanes in the water by HRGC-ECD

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ABSTRACT. The development and validation of a simultaneous liquid-liquid extraction method for organochlorine pesticides and trihalomethanes in surface and drinking water by HRGC-ECD is described. The method presents acceptable recovery, with detection ranging from 2.7 to 49.0 ng L^{-1} for organochlorine pesticides and from 18.0 to 860.0 ng L^{-1} for trihalomethanes. The extraction method also presents excellent linearity for all the analytes, with excellent repeatability. Extraction is simple, fast, and low cost, uses small amounts of solvent and aqueous sample, and is suitable for routine analyses.

Key words: extraction, gas chromatography, organochlorine pesticides, trihalomethanes, water.

RESUMO. Desenvolvimento e validação de método para a determinação de pesticidas organoclorados e trihalometanos em água usando HRGC-ECD. O presente trabalho trata do desenvolvimento e validação de um método de extração para a determinação simultânea de trihalometanos e pesticidas organoclorados em água superficial e água potável por HRGC-ECD. O método apresenta recuperação aceitável, com limites de detecção que variam de 2,7 a 49,0 ng L^{-1} para pesticidas organoclorados e de 18,0 a 860,0 ng L^{-1} para trihalometanos. O método de extração apresenta também excelente linearidade para todos os analitos e boa repetibilidade. A extração é simples, rápida, de baixo custo, além de utilizar pequenas quantidades de solvente e de amostra aquosa, sendo, portanto, de alta aplicabilidade em análises de rotina.

Palavras-chave: extração, cromatografia, pesticidas organoclorados, trihalometanos, água.

Introduction

Organochlorine pesticides and trihalomethanes are chemical substances presenting health and environmental risks; therefore, their levels of concentration in drinking and surface water must be monitored. In Brazil, there are two regulations that establish acceptable levels: Ministry of Health regulation n° 518/2004, specifically for the control and monitoring of organochlorine pesticides and trihalomethanes in drinking water, and regulation n° 357/2005, from Conama, the National Environmental Council, which establishes maximum levels for organochlorine pesticides in surface water.

Organochlorine pesticides (OCP) are synthetic chemicals and are among the most persistent pollutants in aqueous environments (BAIRD, 2002). Due to their chronic persistence and bioaccumulation, they have been banned or restricted for some applications, and most of them have been included in the list of priority pollutants in many countries. Several studies have shown that organochlorine pesticides have deleterious effects on the immune system and increased amounts have been detected in certain cancerous tissues (KRIEGER et al., 1994). Organochlorine pesticides have been reported as possibly responsible for stimulating the development of breast cancers in women (FALCK et al., 1992) and in male mice normally resistant to breast cancer (DAVIS et al., 1993). The risk of breast cancer has been related to the possible interaction between organochlorine pesticides and estrogen receptors (JAGA, 2000).

In Brazil, the Ministry of Agriculture also regulates the registration of active ingredients for various uses in agriculture. The use of organochlorine pesticides has been restricted since 1986. However, four active principles from this pesticide group are still registered in Brazil. These are dicofol, endosulphan, methoxychlor and lindane. Dicofol and endossulfan are still used on cotton, coffee, soy bean, citrus and apple crops. Besides the use of allowed organochlorine pesticides, forbidden organochlorine pesticides are still commonly

smuggled into Brazil, demonstrating the importance of evaluating these compounds in surface and drinking water and in the entire environment.

Other chemical compounds detected in drinking water and as dangerous to the health as organochlorine pesticides are trihalomethanes (THM). Trihalomethanes are represented by chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$) and bromoform ($CHBr_3$). The formation of THM in drinking water results from the reaction of chlorine with naturally occurring organic matter present in surface water, mainly humic and fulvic acids. The Brazilian drinking water quality standard for total trihalomethanes (THM) is 100 μg L^{-1}. Chlorine is applied to drinking water in order to deactivate microorganisms and/or to ensure a residual concentration in drinking water distribution system avoid the development of microorganisms. It has traditionally been a preferred disinfecting agent due to its effectiveness and relatively low price (RODRIGUEZ; SERODES, 2001).

The presence of chlorinated disinfection by-products (DBP), especially THM, in drinking water is of concern from a public health standpoint, because they are suspected to be carcinogenic (TOKMAK et al., 2004). Several studies have suggested that there are increased risks of bladder, stomach, large intestine, and rectal cancer in areas where chlorinated surface waters have been used (LEE et al., 2001).

Organochlorine pesticides and THM are present in water at residual levels. Sample preconcentration is necessary for later chromatographic analysis. Several methods for the determination of organochlorine pesticides and THM in water have been developed and reported in the literature, such as liquid-liquid extraction: LLE; purge-and-trap: PAT (DIAMADOPOULOS et al., 1998) direct aqueous injection: DAI; and headspace: HS (CASTELLO et al., 1986). Goufinopoulos et al. (2001), verified that HS and PAT were more sensitive than DAI e LLE. The advantages of utilizing HS or PAT include minimal sample preparation, reproducibility, reduced analysis times using an automated system, and the possibility of on-line coupling to a GC. However, disadvantages include matrix effects for HS and the higher prime cost and carryover problems with PAT (FATOKI; AWOFOLU, 2003).

In addition to LLE, solid phase extraction (SPE) has been used to analyze organochlorine pesticides in surface water, generally with cartridges packed with silica sorbents modified with octadecylsilyl. This technique uses a smaller amount of solvent and is less laborious than conventional liquid-liquid extraction. However, disadvantages include significant background interference and poor reproducibility (CASTELLO et al., 1986).

An advantage of solid phase micro extraction (SPME) for organochlorine pesticide extraction in water samples is the absence of solvent, and excellent sensitivity and reproducibility (GOLFINOPOULOS et al., 2001). However, the fibers are fragile and expensive, and some pesticides, such as DDT and endrin, suffer thermal decomposition inside the fibers.

A new extraction technique based on the same extraction principles as SPME was developed (BALTUSSEN et al., 1999). A stir bar is coated with the sorbent polydimethylsiloxane (PDMS). This technique is known as stir bar sorptive extraction (SBSE) and the coated stir bars are sold under the Twister name. However, this method is difficult to apply in routine analysis.

Liquid-phase micro-extraction is an emerging extraction technique with applications in biomedical, environmental and food analysis (PSILLAKIS; KALOGERAKIS, 2003). LPME uses a hollow polypropylene fiber which is impregnated with microliters of a nonpolar solvent (toluene, n-hexane, dichloromethane or isooctane) and connected to a microsyringe. Later, the solvent along with the dissolved analytes is sucked into the microsyringe, for chromatographic analysis. LPME is a more reproductive technique than SPME. It requires smaller amounts of solvent, but to achieve highly efficient extractions, the analytes must present low water solubility, low volatility and high stability in the fiber pores. Direct LPME has not been reported in the literature for THM analysis. However, Zhao and Lee (2001), had good THM recovery using headspace coupled with LPME (HS-LPME) with limits of detection (LOD) ranging from 0.15 to 0.4 μg L^{-1}.

Liquid-liquid extraction (LLE) is the most commonly used method for water sample preparation. EPA Method 508 and EPA Method 551.1 are official methods for analyzing organochlorine pesticides and THM, respectively, and may be carried out manually by shaking the water sample and an organic solvent in a separation funnel, or automatically with a continuous liquid-liquid extractor. EPA Method 508 uses methylene chloride as an extraction solvent, EPA Method 551.1 uses methyl-*tert*-butyl ether (MTBE) and pentane to extract THM and five organochlorine pesticides in drinking water samples, with manual shaking.

Dichloromethane needs to be removed in evaporation stages, however, and this may overload the electron capture detector. Moreover, many extraction stages increase the possibility of sample contamination and make the process slow and tedious.

Having analyzed the advantages and the disadvantages of each extraction method available for the analysis of THM and organochlorine pesticides in water samples, we now propose a simple and inexpensive automated liquid-liquid extraction technique which can be applied in routine analyses of water quality.

Material and methods

Chemicals

Organochlorine pesticide analytical standards Lindane (99%), Aldrin (99%), Dieldrin (99%), Endosulphan (96.6%), Endrin (77.3%), *o,p´*-DDT (99%), DDD (72.9%), *p,p'*-DDE (99%) and Metoxychlor (99%) were purchased from PolyScience (Niles, IL, USA). Mirex (99%), α-chlordane (99%), λ-chlordane (99%) and hexachlorobenzene (HCB) (99%) were EPA standards.

Standard solutions of 200 mg L^{-1} of THM in methanol, including chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$), were purchased from AccuStandard® (New Haven, USA).

Hexane and acetone for ultra resi-analysed® and Absolv® were obtained from J.T. Baker® and Tedia®, respectively. Sodium chloride was purchased from Mallinckrodt Baker (Xalostoc, Edo. de Mex, Mexico). Ultrapure water was prepared by purifying demineralized water using a Milli-Q filtration system (Millipore, Bedford, USA).

Stock and spiking solutions

Stock solutions of organochlorine pesticides were prepared in hexane (10.0 mg L^{-1}). These solutions were diluted as required to prepare intermediate stock solutions. Solutions to obtain the calibration curve were prepared by dilution of working solutions in the following concentrations: aldrin and dieldrin (0.24 - 0.36 μg L^{-1}), o,p´-DDT, DDD, p,p´-DDE and Lindane (16 - 24 μg L^{-1}), Methoxychlor and Endosulphan (160 - 240 μg L^{-1}), Endrin (4.8 - 7.2 μg L^{-1}), Hexachlorobenzene (8.0 - 12 μg L^{-1}), Mirex (0.8 - 1.2 μg L^{-1}), α-chlordane and λ-chlordane (1.6 - 2.4 μg L^{-1}).

Acetone was used to prepare the spiking stock solutions of pesticide standards (10.0 mg L^{-1}) to contaminate ultrapure water. Aliquots of the spiking stock solutions were diluted to prepare intermediate spiking solutions in acetone in their final concentration. Aliquots collected to prepare working calibration standards used in LLE experiments were around 100 μL. All of these stock and spiking solutions were stored in a freezer.

The solutions to obtain the THM curve calibration were prepared by diluting the stock solution in hexane at concentrations that varied around the limit of detection (LOD) for each THM and 1,500 μg L^{-1}.

Liquid-liquid extraction procedure

The liquid-liquid extraction was performed using a basic VXR model IKA® Vibrax® orbital shaker, with a 21 mm-diameter test tube attachment. A water sample aliquot (20 mL) was transferred to a test tube fitted with a stopper. Prior to the extraction, 3% (w v^{-1}) sodium chloride was added to all water samples. The extraction was carried out after adding an aliquot of hexane (2 mL) by shaking the test tube at 1,400 rpm for 2h. The phases were then allowed to separate and the organic layer was analyzed by HRGC-ECD.

Extraction efficiency

OCP was extracted by the LLE method by spiking OCP standards in ultrapure water at five levels of concentration. Water samples (100 mL) were spiked with solutions of pesticides in acetone in concentrations as shown in Table 1. The ratio of the amount of OCP recovered from spiked water samples to the amount added to spike was used to calculate OCP recovery in fortified water samples, based on the ratio of the peak areas of the standards to the working calibration solution with the same concentration.

Table 1. Concentration levels of water samples spiked with organochlorine pesticides for recovery studies.

Pesticides	Concentration levels (μg L^{-1})				
	1	2	3	4	5
Hexachlorobenzene	0.8	0.9	1.0	1.1	1.2
Lindane	1.6	1.8	2.0	2.2	2.4
Aldrin	0.024	0.027	0.030	0.033	0.036
λ-chlordane	0.16	0.18	0.20	0.22	0.24
Endosulphan	16	18	20	22	24
α-chlordane	0.16	0.18	0.20	0.22	0.24
Dieldrin	0.024	0.027	0.030	0.033	0.036
p,p'-DDE	1.6	1.8	2.0	2.2	2.4
Endrin	0.48	0.54	0.60	0.66	0.72
DDD	1.6	1.8	2.0	2.2	2.4
o,p´-DDT	1.6	1.8	2.0	2.2	2.4
Metoxychlor	16	18	20	22	24
Mirex	0.08	0.09	0.1	0.12	0.14

Some parameters were evaluated to improve extraction efficiency, such as the effects of adding

NaCl to the samples and the time of extraction. The concentration of pesticides for this evaluation was the maximum allowed by Brazilian legislation.

For THM extraction efficiency studies, the best extraction time and NaCl content parameters for organochlorine pesticides were selected. Concentration levels to evaluate THM recovery were 50, 75, 100, 125 and 150 μg L^{-1}.

Instrumentation

Chromatographic analysis of organochlorine pesticides and trihalomethanes was performed on a Hewlett-Packard 6890 Series Gas Chromatograph equipped with a ^{63}Ni electron capture detector (ECD) system. A HP-5 capillary column (Agilent Technologies) and cross linked 5% phenyl methyl siloxane, 30 m x 0.25 mm I.D. x 0.25 μm, were used for all investigations. The injector was used in pressure-pulsed splitless mode. Purge flow to split vent and injection pulse pressure were evaluated. The injector and detector were kept at 220ºC and 300°C, respectively. The oven temperature was initially 40°C and was then increased at 20°C $min.^{-1}$ to 190°C and kept at this temperature for 7 min.; following this, the temperature was ramped at 20°C $min.^{-1}$ to 220°C and was held for 5 min., and finally a third ramp to 280°C at 30°C $min.^{-1}$ was applied, with the final temperature held for 3 min. 1 μL aliquots were injected manually with a microsyringe.

Results and discussion

Chromatographic analysis

The Figure 1 shows the chromatographic profile obtained for THM and OCP after liquid-liquid extraction of water samples spiked with OCP and THM standards at the maximum concentration level allowed by Brazilian legislation (level three, as shown in Table 1). The chromatogram shows good separation of the analytes with acceptable analysis time and good sensitivity, demonstrating that the chromatographic conditions are excellent for the separation and simultaneous determination of THM and OCP.

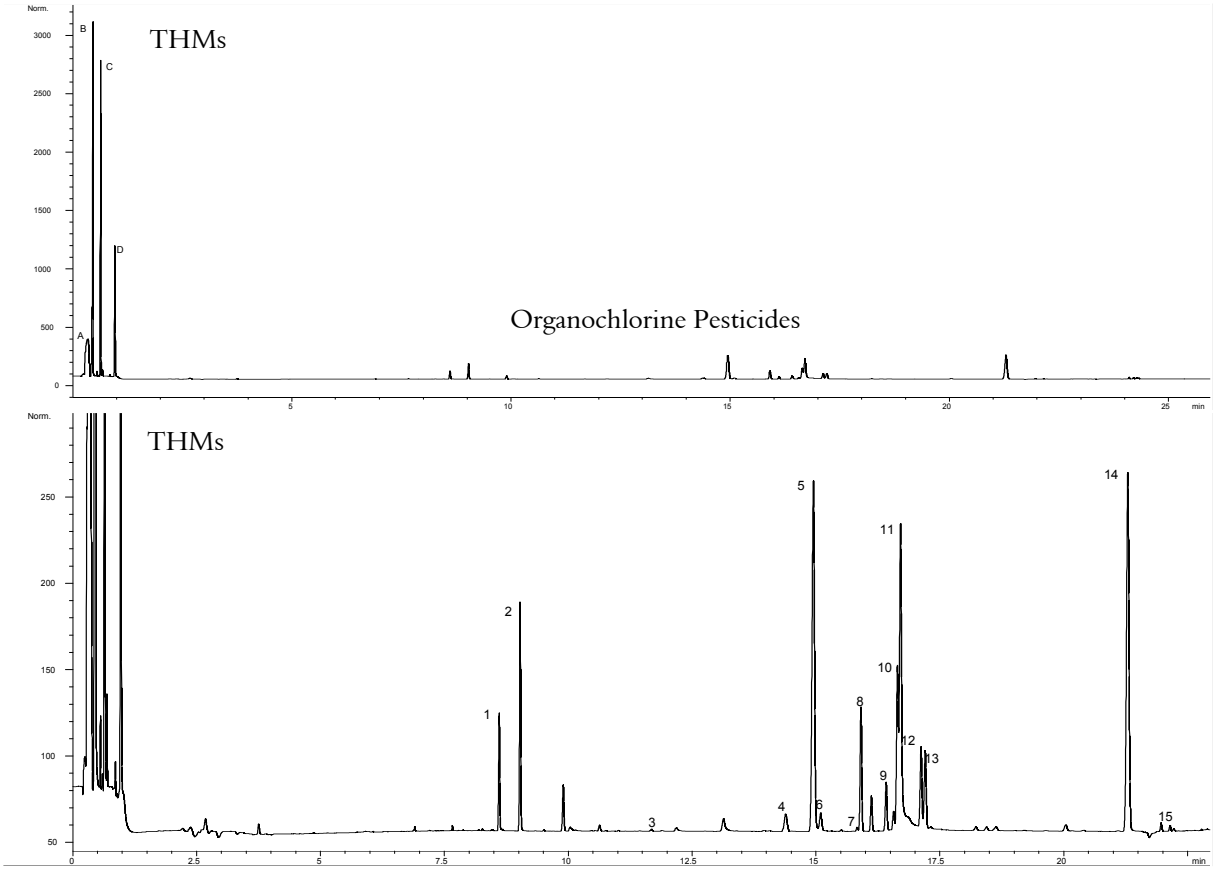

Figure 1. Chromatograms for THM and OCP simultaneous determination by automated liquid-liquid extraction and chromatographic analysis by HRGC-ECD. Peaks: 1) Hexachlorobenzene, 2) Lindane, 3) Aldrin, 4) λ-chlordane, 5) Endosulphan I, 6) α-chlordane, 7) Dieldrin, 8) p,p´-DDE, 9) Endrin, 10) Endosulphan sulphate, 11) Endosulphan II, 12) DDD, 13) o,p´-DDT, 14) Mehoxychlor, 15) Mirex. A) $CHCl_3$, B) $CHCl_2Br$, C) CHClBr.

Optimization of LLE conditions

Salting-out effect

The effect of added NaCl in the recovery efficiency of organochlorine pesticides in water samples was investigated, with results shown in Figure 2. The o,p´-DDT, p,p´-DDE and hexachlorobenzene showed better extraction efficiency in an NaCl concentration of 1% (w v^{-1}). Aldrin did not present good extraction at NaCl concentrations lower than 10% (w v^{-1}). An increase in saline concentration did not affect the extraction of dieldrin. Endrin, α-chlordane, λ-chlordane, mirex, endosulphan, metoxychlor, lindane and DDD showed better extraction in NaCl concentrations of 3% (w v^{-1}). Thus, the concentration of NaCl used in the experiments was 3% (w v^{-1}) because it allowed acceptable extraction yield for most analytes.

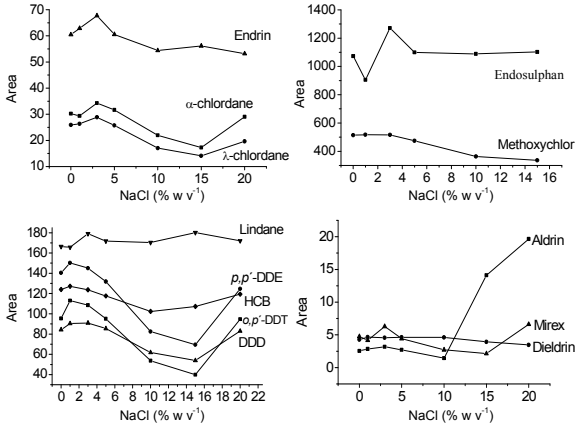

Figure 2. Effect of NaCl concentration on the extraction of organochlorine pesticides from water samples.

Extraction time

The Figure 3 shows the peak area obtained by HRGC-ECD for OCP as a function of extraction time. This evaluation shows that the majority of the analytes present a constant peak area in extraction time of 30 min., and these values have practically no variation when extraction time is increased, except for aldrin, which is extracted in higher amounts from water samples when the extraction time increases.

The Table 2, which presents OCP recovery as a function of extraction time, shows that in 30 min., most analytes presented satisfactory recovery, except for aldrin and dieldrin. Considering that Brazilian legislation still allows aldrin to be used under certain conditions, pesticide recovery was also evaluated over longer extraction times in an attempt to improve the extraction of aldrin and dieldrin.

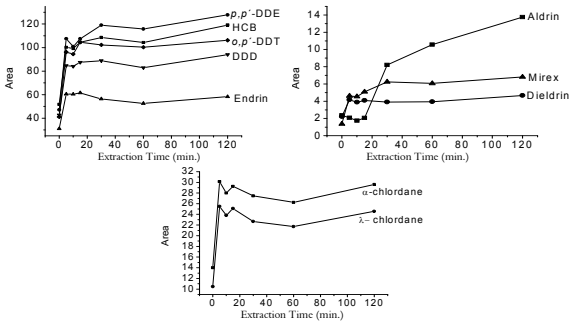

Figure 3. Effect of extraction time on the recovery of OCP from water.

Table 2. Mean recoveries and precision for OCP with the proposed LLE method as a function of extraction time.

Pesticides	Extraction time		
	30 min.	120 min.	180 min.
	Percentage of Recovery (RSD %)[a]		
HCB	98.6% (7.6)	92.5% (6.6)	90.4% (4.4)
Lindane	100.0% (1.2)	116.5% (15.2)	118.1% (13.3)
Aldrin	29.9% (16.2)	50.0% (16.8)	39.0% (3.7)
λ-chlordane	90.0% (6.1)	104.8% (4.4)	88.2% (8.8)
Endosulphan	85.1% (4.9)	110.6% (4.9)	108.3% (4.9)
α-chlordane	89.0% (5.2)	101.5% (8.9)	94.8% (7.9)
Dieldrin	27.6% (16.4)	64.8% (3.7)	63.5% (2.0)
p,p´-DDE	60.8% (2.5)	75.2% (4.7)	67.5% (5.6)
Endrin	94.4% (7.2)	110.4% (5.2)	110.3% (5.2)
DDD	84.3% (5.2)	90.1% (1.6)	82.8% (6.6)
o.p´-DDT	82.7% (12.1)	85.5% (5.8)	75.3% (4.4)
Metoxychlor	65.5% (4.7)	107.3% (8.7)	100.0% (6.4)
Mirex	74.4% (8.2)	60.8% (16.5)	46.6% (9.5)

[a]Obtained for five determinations.

With an increase in extraction time to 120 min., aldrin and dieldrin were extracted at higher levels. When the extraction time was increased to 180 min., the recovery levels decreased again. This was also observed for other OCPs. Mirex always demonstrates a reduction in recovery with an increase in extraction time.

Thus, the extraction time that promoted the best recovery of the analytes in water was 120 min., with recovery ranging of 50.0% for aldrin and 116.5% for lindane. The relative standard deviation (RSD) varied between 1.6% for DDD and 16.8% for aldrin. These results demonstrate that this extraction method appears to promote acceptable recovery with good repeatability.

The efficiency and accuracy of the extraction method under discussion was also evaluated using quality parameters such as linearity, precision and sensibility. Under optimum conditions, linearity, limit of detection, limit of quantitation and repeatability data were obtained and shown in Table 3.

All organochlorine pesticides exhibited good linearity with correlation coefficients (*r*) of 0.99072-0.99905. This allowed the quantitation of these compounds by the external standardization method.

Table 3. Linearity, precision and limits of detection and quantitation for the analysis of OCP.

Pesticides	Coefficient of Correlation (*r*)	RSD (%) n=3	LD (μg L^{-1})	LQ (μg L^{-1})
HCB	0.99602	2.200	0.0050	0.0150
Lindane	0.99496	2.100	0.0470	0.1400
Aldrin	0.99867	0.099	0.0038	0.0077
λ-chlordane	0.99083	0.056	0.0037	0.0095
Endosulphan	0.99905	6.800	0.0120	0.0300
α-chlordane	0.99368	0.380	0.0029	0.0059
Dieldrin	0.99072	0.260	0.0035	0.0087
p.p´-DDE	0.99644	2.680	0.0027	0.0067
Endrin	0.99675	0.860	0.0086	0.0170
DDD	0.99880	1.200	0.0035	0.0087
o.p´-DDT	0.99621	0.750	0.0030	0.0060
Methoxychlor	0.99564	11.000	0.0095	0.0190
Mirex	0.99195	0.150	0.0035	0.0070

Limits of detection (LOD) of the OCP, calculated on the basis of the signal to noise (s/n) ratio of 3 in HRGC-ECD measurements, were in the range of 0.0027-0.0470. The limit of quantitation (LOQ) was established as the lowest concentration that has a relative standard deviation of 20% and varied between 0.0059 μg L^{-1} for α-chlordane and 0.1400 μg L^{-1} for lindane. Repeatability was evaluated by extracting aqueous sample spiked at five levels of concentration for each OCP with three replicates. The relative standard deviations (RSD) were acceptable, ranging from 0.056 to 11.000%.

THM analysis

The same optimized extraction conditions obtained for organochlorine pesticides were used for trihalomethanes analysis. THM extraction efficiency was evaluated as shown in Table 4, which indicates that mean recovery varied from 78.9% for $CHCl_3$ to 93.2% for $CHBr_3$. All THMs exhibited good linearity with correlation coefficients (r) of 0.99423-0.99949, allowing the quantitation of these compounds by external standardization.

Table 4. Recovery, linearity, precision, limits of detection (LOD) and quantitation (LOQ) for the analysis of THM.

THM	Recovery (%) (RSD)	(*r*)	Calibration Curve	RSD (%) (n=3)	LOD (μg L^{-1})	LOQ (μg L^{-1})
$CHCl_3$	78.9 (11.6)	0.99949	$\hat{y}$ =1052.54x + 15.71	2.5	0.018	0.052
$CHCl_2Br$	87.5 (5.8)	0.99820	$\hat{y}$ =2745.67x + 65.41	1.9	0.26	0.39
$CHClBr_2$	88.1 (8.7)	0.99423	$\hat{y}$ =1728.85x + 61.21	2.8	0.035	0.052
$CHBr_3$	93.2 (3.5)	0.99720	$\hat{y}$ =954.81x + 38.15	3.4	0.86	1.3

(*r*) Coefficient of Correlation.

Limits of detection (LOD) for THM, calculated on the basis of the signal to noise (s/n) ratio of 3 in HRGC-ECD measurements, were in the range of 0.018 - 0.260 μg L^{-1}. The relative standard deviations (RSD) were in the range of 1.9 - 3.4%, demonstrating that the method possesses high sensitivity and good repeatability.

Conclusion

This paper demonstrates the successful development and application of an automated liquid-liquid extraction method. The method exhibits good precision, reproducibility and linear response over a wide concentration range, demonstrating the possibility of simultaneous determination of trihalomethanes and OCP by high resolution gas chromatography. The method allows fast and easy sample preparation for routine analysis, without extract evaporation stages or sample clean-up. This reduces problems of interference over many stages of sample manipulation. Due to the automation of the extraction and the use of small amounts of solvent, the exposure of the analyst to toxic solvents was avoided. Moreover, the method is not tedious, and it is possible to prepare up to sixteen samples simultaneously. Thus, the method developed is viable, fast and low cost for routine analysis of trihalomethanes and organochlorine pesticides in water by trace analysis and water quality control laboratories.

Acknowledgements

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