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Monitoring organochlorine pesticides from landfill leachates by gas chromatography–electron-capture detection after solid-phase microextraction☆

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Abstract

Landfill leachates contain significant amounts of organic carbon, nitrogen and heavy metals as well as other specific trace organic compounds like organochlorine pesticides. In this study a simple and reliable methodology was improved to detect organochlorine pesticides in leachate samples by using a previous solid-phase microextraction procedure [with a 100 μm poly(dimethylsiloxane) fiber] and chromatographic analysis by GC–electron-capture detection. The extraction time, temperature, ionic strength of the solution and sampling of the headspace were the parameters studied. Reproducibility achieved values below 20% RSD, and standard addition was used for pesticides confirmation.

Keywords: Environmental analysis; Pesticides; Organochlorine compounds

1. Introduction

Organic compounds are the most representative constituents of municipal landfill leachates. They are the result of the biological activity of landfill residues. Their chemical characteristics depend on the landfill age [1]. Difficulties of treatment arise frequently from the fact that some highly toxic organic compounds present in leachates may inhibit biological water treatment stages. Among them, organochlorine pesticides, polychlorinated biphenyls (PCBs) and chlorinated solvents claim for special attention as long as their final destination is surface water. Thus it is extremely important to be able to quantify this strongly impact traces, most of them listed in ''red'' or ''black lists'' in the USA and Europe [2].

The instrumental analysis used to detect most of the organic traces is being continuously improved by increasing the detection capacity of the huge variety of compounds in environmental samples. Also the techniques to prepare these samples are evolving towards simpler and more reliable methods, where an increasing concern due to the use of extraction solvents is laying aside some of the classical liquid–liquid methodologies.

Solid phase microextraction (SPME) is an

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extraction methodology recently developed, that is useful for extracting pesticides from aqueous samples due to its simplicity and solventless procedure [3–5].

Since the beginning SPME has offered a wide range of applications. Initial studies addressed the determination of volatile organic compounds in aqueous samples [6], but the SPME application to the extraction of pesticides is proving to be an effective alternative to the traditional time-consuming extraction techniques. Organochlorine pesticides [5,7,8], organophosphate pesticides [9–11], nitrogen-containing herbicides [3,4,12–14] and polychlorobiphenyls [15] are examples of SPME application to environmental samples.

Fibers used by SPME to extract the analytes differ among each other by their coating and thickness, which influence the analytes sorption, but other factors like sorption and desorption times, temperatures, rate of stirring, pH and ionic strength of the sample also play an important role on the process [16].

The aim of this work is to validate an analytical methodology whose purpose is the detection of organochlorine pesticides in some hazardous samples, leachates from sanitary landfills. Although most of experimental SPME conditions described in the literature use fiber immersion for organochlorine analyses [5], this work intends to study the possibility of using the headspace sampling, where the organic interferences coming from a complex matrix as a leachate are expected to be reduced.

If sampling is performed in the headspace, the decrease in the volume occupied by the vapour phase will increase the partial pressure of the compounds in this phase, thus implying that better results should be expected having a lower proportion between the volume of aqueous and vapour phases [6,7]. Experimentally, the sampling should be done in vials that allow a representative sampling volume and a correspondent headspace as little as possible but still allowing the fiber exposure to the vapour phase. A drawback of this technique is the need to ensure a perfectly tightly closed system. Nevertheless headspace sampling is the right choice when samples exhibit undissolved particles or low volatile compounds, which may interfere, either in the chromatographic analysis or competing to the adsorption sites of the fiber. For example, Page et al. [7] presented a suitable methodology for the analysis of organochlorine pesticides in aqueous samples, suggesting that for a 15-ml sample volume, 30-ml vials with 45 min extraction time are used, and for 110-ml sample volumes, 125-ml vials and extractions times of 60 min are used. In both cases the extraction was carried from the headspace at 87°C.

In this study, the implementation and validatation of a simple extraction methodology (SPME) and chromatographic determination [gas chromatography–electron capture detector (GC–ECD)], suitable to be used routinely by quality control laboratories as a valuable tool for monitoring pesticides whenever a more specialised analytical methodology such as GC–MS is not always available, was intended.

2. Experimental

2.1. Chemicals

The nine chlorinated pesticides – lindane (LIN), purity=99%; heptachlor (HEP), purity=99%; aldrin (ALD), purity=99%; dieldrin (DIE), purity=99%; endrin (END), purity=99%; endossulfan (ENS), purity=96%; DDE, purity=99%; DDD, purity=70% and DDT, purity=99% – were obtained from Poly-Science (kit 510CX). Water was deionised and distilled. Hexane was used as the solvent, and other common reagents were of analytical grade.

2.2. Chromatographic equipment and experimental conditions

The chromatograph was an HP5890 equipped with a ^{63}Ni electron-capture detection (ECD) system connected to a computerised data acquisition system provided with an Datapex software. Chromatographic separation was performed with a HP-PAS 1701 capillary column (25 m×0.32 mm I.D.×25 μm film). The carrier and make-up gases were argon–methane (95:5) at 2.80 ml/min and 50 ml/min, respectively. The split/splitless injector and detector

temperatures were 250 and 300°C, respectively. The initial oven temperature was kept at 80°C for 1 min and afterwards programmed to 210°C at a rate of 35°C/min, held for 4 min, then raised to 240°C at 5°C/min, kept for 2 min, finally raised to 270°C at 10°/min and held for 2 min. To determine the linearity of the instrumental analysis, the standards of organochlorine pesticides were prepared in *n*-Hexane and 1-μl volumes were injected.

2.3. SPME equipment and experimental conditions

The 100-μm poly(dimethylsiloxane) (PDMS) fiber and respective assembly were obtained from Supelco. The fiber was conditioned in the GC injector for 1 h at 250°C. Whenever needed, this procedure was repeated for fiber clean-up. Before the sample extraction, blank runs were performed to look for fiber contamination.

A working standard containing the nine organochlorine pesticides at a mean concentration of 300 mg/l was prepared with ethanol and then diluted with water in order to obtain aqueous standards at an average concentration of 3 mg/l. The vial capacity was 15 ml, handling 7.50 ml of sample. Both temperature and stirring velocity were controlled during the extraction. Optimised extraction conditions were: headspace sampling at 55°C over 30 min, with a PDMS 100-μm fiber and without salt addition. After the extraction, the fiber assembly was inserted in the injector, through the septum, and pushed until its end remained about 1 cm above the injector surface. The fiber remained in the injector for 3 min with the split valve closed at 250°C. Intermediate blank runs were periodically performed to check the carry-over.

2.4. Quantification

Pesticides were quantified by peak area using the external standard method. A calibration curve was obtained with eight organochlorine standards in the range from 0.1 to 20.0 μg/l, extracted in the same conditions as the samples were. Confirmation of the detected analytes was performed by standard addition at three concentration levels.

3. Results and discussion

3.1. SPME optimisation

Experimental conditions, such as the equilibrium time, the fiber exposure to the vapour or liquid phase, the salt interference or the temperature, were previously optimised before validating the analytical methodology. Stirring is also important to generate a continuously fresh surface in order to improve the extraction [16] because the static layer resistant to mass transfer is destroyed. In this study all the experiments were performed under a controlled stirring velocity.

3.2. Extraction time

When analytes have low Henry's constant values, low concentrations at the vapour phase are expected, thus translated on a small concentration gradient and so there is a subsequent need for longer periods to reach the equilibrium. Also high molecular mass analytes are expected to have longer equilibrium times, due to their lower diffusion coefficient (the equilibrium time is inversely proportional to the diffusion coefficient) [17]. In most cases the equilibrium is established when 90% of the final value is reached. If this option is adopted to shorten the analysis time, it is very important to ensure a reproducible sampling time in order to obtain reproducible results.

When complex samples with different affinities to the fiber coating are to be extracted, a compromise must be established. In the present study, the data in the literature [18] report relatively small Henry constants, K_H, for most of the organochlorines, but large octanol–water partition coefficients, K_{ow}, meaning an expectation of longer equilibrium times necessary to achieve higher extraction efficiencies.

The extraction efficiency of a standard solution was compared for two distinct extraction times – 30 and 75 min (Fig. 1). Extraction was not significantly improved on most pesticides when the extraction time was increased to 75 min, and attending to the fact that the time of analysis was greatly sacrificed, it was decided to keep an extraction time of 30 min in subsequent analysis.

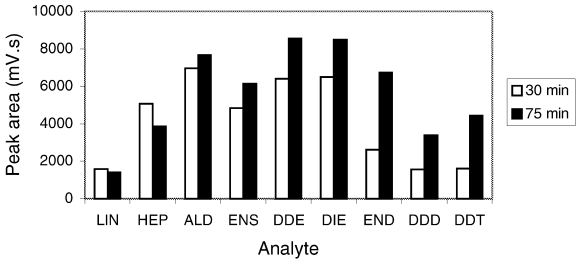

Fig. 1. Effect of the extraction time on SPME extent (100-μm PDMS fiber; headspace; temperature=55°C; standard=1 μg/l).

3.3. Extraction in the headspace versus immersion

Two experiments with aqueous samples spiked with the standard solution of pesticides were performed for a further comparison of the two sampling modes (Fig. 2), which led to the conclusion that the extraction efficiency was significantly improved for ALD, HEP and LIN, compounds with lower molecular masses. For the remaining pesticides, the headspace sampling mode proved to be a suitable technique.

3.4. Effect of the temperature

Fig. 3 reports the results obtained with two experiments performed with the standard solution of pesticides to compare the effect of two distinct temperatures – 20°C and 55°C – in the extraction yield. Attending to the expected behaviour of the pesticides, increasing the temperature improved the mobility of the molecules through the phases and most of the pesticides studied had better recoveries at

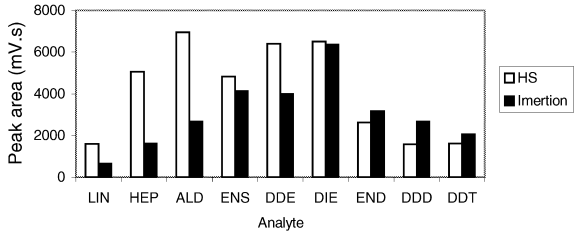

Fig. 2. Comparison of extraction extent (expressed by peak area) between headspace (HS) and immersion sampling (100 μm PDMS fiber; temperature=55°C; time=30 min; standard=1 μg/l).

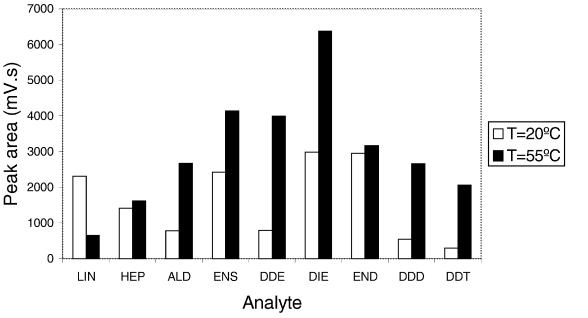

Fig. 3. Influence of temperature in the extraction extent (100 μm PDMS fiber; headspace; time=30 min; standard=1 μg/l).

55°C rather than 20°C. Thus, the temperature of 55°C was definitely chosen for subsequent assays.

3.5. Effect of the ionic strength

Matrix effects as its ionic strength can also influence the mechanism of mass transfer. The sample pH or salt content decreases the solubility of the organic compounds in the water, thus improving the absorption by the fiber coating. Aguilar et al. [13] mentioned that this behaviour is felt especially for analytes with low hydrophobicity. Experiments done with a different salt concentration (NaCl) added to a standard solution (Fig. 4) corroborate this statement because only LIN (considered the most polar of all the organochlorine pesticides in the study) seemed to be more absorbed by the fiber in the presence of a saturated NaCl solution. When using higher NaCl levels, the recovery rate was not significantly improved with the other pesticides. In some cases – like ALD, DDE, DDD and DDT – this rate had even decreased.

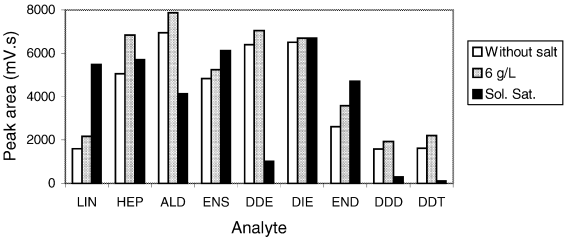

Fig. 4. Effect of salt concentration in the extraction extent (100 μm PDMS fiber; headspace; temperature=55°C; time=30 min; standard=1 μg/l).

3.6. Validation parameters of the analytical methodology

The linearity of the detector response was verified in the range of each pesticide concentration between 0.073 and 17.493 mg/l. Based on the lowest detectable peak with a signal-to-noise ratio of 3, the detection limits were 0.067 mg/l, on average, with a minimum of 0.042 mg/l for HEP and a maximum of 0.105 mg/l for ENS.

The chromatographic time of analysis was 25 min. The intralaboratorial reproducibility was 7.0%, on average, expressed by the relative standard deviation (RSD) obtained on six independent analysis of the standard solution. The repeatability was 6.6%, on average calculated from five replicates. For both precision parameters, the maximum value was near 10% for LIN and the minimum was 4% for END.

Optimised SPME conditions were: headspace sampling at 55°C over 30 min with a PDMS 100-μm fiber, without salt addition. For accounting the extraction efficiencies, it was decided to use the calibration curves obtained with the extracted standards (Fig. 5) in order to quantify the pesticides. Detection limits obtained from the calibration curves were 0.1 μg/l on average. The pesticides standard solutions levels ranged from 0.1 to 5.9 μg/l on average. The SPME repeatability was determined from seven extractions of 1 μg/l spiked solutions of all the pesticides, and the RSD ranged between

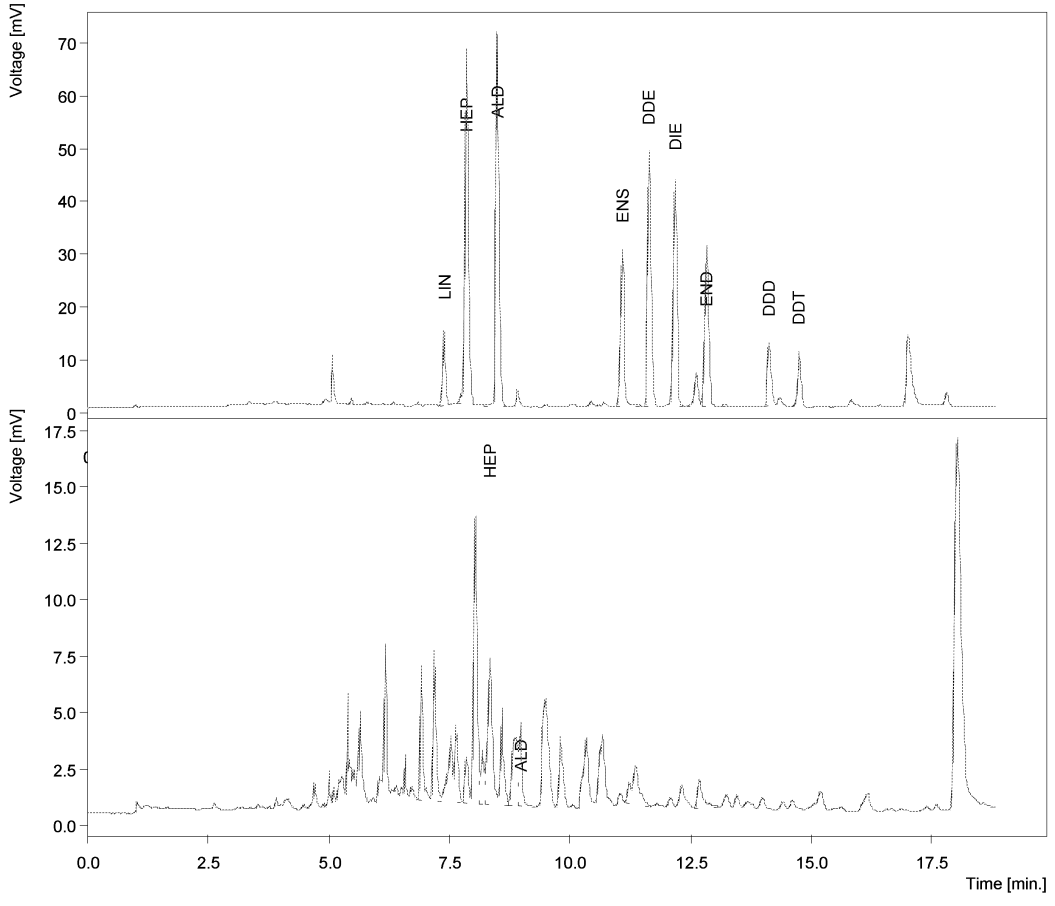

Fig. 5. Chromatograms of (upper) extracted pesticides standard solution 1 μg/l on average (LIN=1.11 μg/l, HEP=1.45 μg/l, ALD=1.13 μg/l, ENS=1.14 μg/l; DDE=1.32 μg/l, DIE=1.15 μg/l, END=1.47 μg/l, DDD=1.15 μg/l, DDT=1.18 μg/l); (lower) leachate with the probable identification of HEP and ALD.

4.74% for ALD and 20.38% for DDT with a mean value of 11.34%. The reproducibility for eight assays had a minimum value of 5.01% for ALD and maximum of 30.44% for DDD with an average of 13.56%. DDE, DDD and DDT presented a RSD above 20%. Recovery was studied for three levels of added standards, and the recovery factor was 78.5% on average.

3.7. Leachates analysis

The samples were collected from three landfills for domestic residue treatment plants. Leachates are complex samples with a strong variety of organic and inorganic compounds, giving a dark colour and an occasional petroleum odour.

Ten leachate samples were collected over a relatively large period of time to verify if the possible detection of an individual pesticide was a scattered or a persistent one. A chemical characterisation of the leachates reported average values of 8.4 for pH, 30 000 μs/cm for conductivity, 4700 mg O_2/l for chemical oxygen demand, 300 mg O_2/l for biochemical oxygen demand, 30 mg/l for total oil and grease and finally 15 mg/l for total hydrocarbons.

The results from the ten leachates analysis showed that DDD, DDT and ENS had not been detected. However, chromatographic peaks had been identified at the same retention time of the other pesticides, most of them below the detection limit.

Great care must be taken in order to avoid erroneous conclusions due to matrix interferences. Two different matrix effects need to be considered: the interference that co-elutes with a pesticide leading to higher concentration than the real one, and the fiber saturation due to a highly concentrated interference leading to lower adsorption of the pesticide and subsequent lower values.

To account for these two factors, a recovery study was planned for some of the samples analysed, which consisted of adding to each sample three different levels of standard pesticides. If saturation occurs a deviation from linearity should be expected and if the co-elution of an interference occurs the pesticide concentration of the sample analysed is not the same as the one obtained by standard addition. As an example, it was possible to identify HEP and ALD in one of the ten leachates (Fig. 5), but ALD was below the detection limit and HEP was not confirmed by the standard addition. In this case it is recommended that a more conclusive technique such as GC–MS should be used.

This fact helps to emphasise the importance of having simpler but reliable methodologies of analysis to monitor large amounts of samples, especially when most of them do not contain pesticide contamination.

4. Conclusions

SPME proved to be a suitable methodology to extract organochlorine samples from aqueous samples. An optimised methodology was developed, which was based on a 100-μm PDMS fiber, headspace sampling mode and an extraction time of 30 min at a temperature of 55°C. The quantification method used calibration curves obtained from standards extracted in the same experimental conditions as the samples, in order to account for the different extraction efficiencies. The validation parameters revealed a satisfactory precision with an average RSD% of 10% and detection limits of 0.1 μg/l. When the spiked samples were analysed, the recovery percentage was 78.5% on average. Special care was taken on the confirmation of the pesticides detected. To reach this purpose, standard addition at three concentration levels was used.

This simple extraction methodology of the GC–ECD analysis can be easily implemented into the routine of quality control laboratories as a valuable tool for monitoring pesticides in landfill leachates.

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