DETERMINATION OF NON HALOGENATED SOLVENTS IN INDUSTRIAL WASTEWATER USING SOLID PHASE MICROEXTRACTION (SPME) AND GC-MS

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Abstract— **Solid phase microextraction (SPME) was applied to the analysis of a selected group of non halogenated solvents -all of them classified as volatile organic compounds (VOCs)- that may be present in diverse industrial wastewaters. Two different fibres (100-PDMS and 85-PA) were selected as SPME adsorbents. The extracted volatile organic compounds were analysed by high resolution gas chromatography coupled to mass spectrometry (GC-MS), following the EPA method 624. Calibration curves and method detection limits obtained for these solvents using the two SPME fibres are reported. The 100-PDMS fibre provided better sensitivity, but the saturation was reached at a lower concentration than 85-PA fibre.**

The first fibre (100-PDMS) was applied to the analysis of several textile wastewaters. The method detection limits obtained with this fibre were: 0.1-0.3 µg/L for ethylbenzene, m-xylene, p-xylene, toluene and diisobutyl ketone. In addition, SPME and Headspace (HS) detection limits were compared.

Keywords— **Solid phase microextraction (SPME), gas chromatography-mass spectrometry (GC-MS), wastewater, industrial solvents, VOCs.**

I. INTRODUCTION

In recent years, there has been a remarkable growth in the number of organic compounds used as solvents for several industrial activities, such as synthesis, extractions, cleaning and protection of surfaces, etc. In general, the industrial processes requiring the use of these compounds include recovery of the used solvents. However, this recovery is hardly ever complete, so part of the solvent is incorporated into the process effluents.

Solvents can be divided into two classes according to their chemical composition: halogenated and non halogenated. In general, the use of halogenated solvents is severely restricted by the regulations of different countries and also by the European Community regulations (Council Directive 89/678/EEC, 1989; Council and European Parliament Directive 94/60/EEC, 1994; Commission Directive 96/55/EC, 1996), since they represent a danger to health and environment.

Non halogenated solvents are increasingly used in industry because of their lower toxicity. However, non halogenated solvents also involve toxicity problems and for this reason, their content in wastewater is also restricted. Moreover, it is important to identify these solvents in industrial wastewater because they could alter the operation of biological treatment plants. Most of these solvents have harmful effects on the environment and are considered priority pollutants by the US Environmental Protection Agency (US-EPA, 2005). They are generally referred as volatile organic compounds (VOCs), which are defined, from a chemical point of view, as organic compounds that have a boiling point ≤100 ºC and/or a vapour pressure >1 mm Hg at 25 ºC. However, the most accepted environmental definition was formulated by the United Nations Commission in 1991 and presented VOCs as organic compounds, different from methane, able to produce photochemical oxidants, mainly ozone, by reaction with nitrogen oxides in the presence of solar light. This category of compounds includes thousands of pollutants; which may have a variety of harmful health effects. At high levels of exposure, many VOCs can cause central nervous system depression. All of them can be irritating upon contact with the skin, or to the mucous membranes when they are inhaled (Jennings and Sneed, 1996).

The most common non halogenated solvents and their main industrial applications are reported in Table 1. Most of them are used as solvents for coatings, resins, paints, plastics, adhesives, printing inks, cosmetics. In the textile industry, they are intermediates in dye synthesis and may also appear as traces or additives in dyes, dye carriers, raw materials and wet textile processing. In pharmaceutical industry, they are mainly employed for synthesis and extraction processes. Another group of compounds is used in the manufacture of plastic fibres, synthetic rubber, artificial leather, photographic films, flavours, perfumes, insecticides, etc (National Safety Council,2004; Spectrum Laboratories Inc., 2004).

In the present work, diverse textile effluents treated in different biological plants were analysed to establish their content in non halogenated solvents. High resolution gas chromatography coupled to mass spectrometry (GC-MS) was employed, following EPA method 624.

Previously, the extraction of solvents was carried out using SPME.

The SPME technique was introduced by Pawliszyn (1997). It is based on the use of a fused-silica fibre coated with a sorbent thin film to extract organic compounds from different matrices (Davoli *et al.*, 2003; Turemis *et al.*, 2003; Rivero and Topiwala, 2004; Francioli *et al.*, 1999) . This technique is useful to isolate volatile compounds from aqueous samples, which cannot be injected directly into the chromatographic system (Nilsson *et al.*, 1997; Deok-Hee *et al.*, 2003). After the extraction, the compounds captured by the fibre are introduced into the GC-MS, where they are separated, identified and quantified.

In this work, the SPME was performed with a headspace configuration HS-SPME: volatile organic compounds were collected in the headspace above the sample, without inserting the fibre into the water matrix (Zhang and Pawliszyn, 1993).

Results corresponding to this technique (HS-SPME) were compared with those obtained by Static Headspace (HS) extraction. The main advantage of SPME and HS extraction techniques is that they do not require the use of solvents and the complete removal of the analytes from the sample, as opposed to traditional sample preparation (solvent extraction). However, for each SPME and HS injection a new extraction must be carried out.

II. EXPERIMENTAL

A. Sample preparation

The solvents selected for analysis are indicated in Table 1. They were supplied by Aldrich (Steinheim, Germany) and Fluka; (Buchs, Switzerland).

Table 1. Non halogenated solvents selected and their industrial application

Compound	C.A.S number	Industrial application
Diethyl ether	60-29-7	Solvent for waxes, oils, perfumes, gums. Plasticiser. Cleansing agent. Surface antiseptic.
Acetone	67-64-1	Cleansing agent in automotive industry. Plastic fibre industry.
Methyl acetate	79-20-9	Solvent for adhesives, paints, cosmetics, cleaning products. Chemical intermediate. Plasticiser.
Methyl ethyl ketone	78-93-3	Solvent for coating, adhesives, printing inks, magnetic tapes. Pesticide formulation.
Ethyl acetate	141-78-6	Solvent for coating, plastics, varnishes, inks. Manufacture of artificial leather, photographic films, flavour fruits.
Tetrahydrofuran	109-99-9	Grignard reaction solvent. Solvent for resins, plastics, printing inks, adhesives, lacquers.
Cyclohexane	110-82-7	Cleaning operations. Solvent for paints, resins, lacquers Fungicidal formulation. Perfume industry.
Benzene	71-43-2	Pharmaceutical synthesis. Dye preparation. Used for printing, paints, rubber, dry cleaning, adhesives, coatings, detergents.
Isopropyl acetate	108-21-4	Coating and cleaning fluids. Solvent for printing inks, fragrances, cosmetics. Personal care products.
2-pentanone	107-87-9	Protective coating. Cleaners. Solvent for synthetic resins
3-pentanone	96-22-0	Intermediate used in perfumery, flavourants, pharmaceuticals, pesticides. Dewaxing agent
Propyl acetate	109-60-4	Formulation of flavours, perfumes, insecticides, inks. Solvent for plastics, resins, lacquers, waxes.
Toluene	108-88-3	Gasoline component. Intermediate in dye synthesis. Paper coating. Solvent in paints, inks, gums, resins and cleaners.
Isobutyl acetate	110-19-0	Used in coating, cleaners, textiles, floor polishes. Extractant for drugs, hormones, vitamins. Additive in gasoline.
Butyl acetate	123-86-4	Manufacture of lacquers, artificial leather, photographic films, plastics, safety glass. Artificial flavouring.
Ethylbenzene	100-41-4	Component of automotive and aviation fuels. Intermediate for styrene production. Solvent in synthetic rubber production.
m,p-xylene	108-38-3/ 106-42-3	Manufacture of polyester fibres Synthesis of dyes, insecticides, motor fuels, pharmaceutical products.
o-xylene	95-47-6	Raw material for plasticisers, resins, pigments. Synthesis of dyes, insecticides, motor fuels, pharmaceutical products.
Diisobutyl ketone	108-83-8	Solvent in paints, coatings, printing inks, adhesives. Leather finishing. Pharmaceutical extraction. Agricultural products.
Nitrobenzene	98-95-3	Synthesis of dyes, perfumes, pesticides, rubber, pharmaceutical products. Manufacture of aniline.

The preparation of the primary external standards was carried out according to the EPA method 624. Standard aqueous solutions of these compounds were prepared from 0.01 mg/L to 5 mg/L. Samples (20 mL) were sealed into a vial with a 10% of sodium chloride in order to improve the migration of the organic solvents towards the vapour phase.

In industrial wastewater samples, an internal standard (toluene d8, 1 mg/L) was added to ensure a more precise relative quantification. This operation was carried out before applying the extraction method.

B. Solid Phase Microextraction (SPME)

Two types of fibre coating were selected for the SPME study: a 100 μm film of poly(dimethylsiloxane) (100-PDMS) and a 85 μm film of polyacrylate (85-PA). A third coating, 7 μm film of poly(dimethylsiloxane), was also tested although it was rejected due to its poor retention of volatile compounds. All fibres were supplied by Supelco (Bellafonte, USA).

Samples were conditioned for 50 minutes (with stirring) into the thermostatic bath before carrying out the extraction. To optimise the solvent extraction, different adsorption temperatures and times ranges were tested (35 ºC-45 ºC and 0.5-15 minutes). After studying results, the selected adsorption conditions were 35 ºC for 10 minutes. Once the volatiles were collected on the fibre from the headspace, the stationary phase was retracted and the syringe was introduced in the chromatographic injector where the thermal desorption occurs.

C. Analysis by Gas Chromatography-Mass Spectrometry (HRGC/MS)

Isolated volatile solvents were analysed with an integrated quadrupole HRGC/MS MD-800 supplied by Fisons (Manchester, UK). The ionisation was performed using EI (Electronic Impact) mode. The acquisition was performed in scan mode (m/z = 35-450 uma). Chromatographic separation was carried out on a DB-624 column (30 m; 0.25 mm ID; 1.4 μm film thickness) supplied by J&W (Folstom, USA). Helium was used as the carrier gas at a pressure of 100 kPa. The oven temperature program was from 50 ºC, (held for 5 min) to 250 ºC (held for 10 min) at a rate of 5 ºC/min. Injector and interface temperatures were 230 ºC. The injection was carried out in splitless mode for 300 seconds. The libraries used for matching were Wiley 6, LIBTX and NIST.

To find the linearity in the method used, 15 standard samples were injected between 0.01 and 5 mg/L. Calibration curves were obtained for each component from the peak areas average of 3 injections. These curves were obtained in two ways for each compound: from areas corresponding to the total ion current (TIC) of the chromatographic peaks and from areas recorded for the main ion mass (m/z) in SIM (Single Ion Monitoring) acquisition mode. Table 2 indicates the selected ion masses of VOCs and their retention time.

Table 2. Selected ion masses and retention times of analysed compounds

Compound	Selected ion mass (m/z)	Retention time (min)
Diethyl ether[1]	59	2.14
Acetone[2]	43	2.36
Methyl acetate[3]	43	2.62
Methyl ethyl ketone[4]	43	4.14
Ethyl acetate[5]	43	4.22
Tetrahydrofuran[6]	42	4.54
Cyclohexane[7]	56	4.97
Benzene[8]	78	5.54
Isopropyl acetate[9]	43	5.75
2-pentanone[10]	43	7.26
3-pentanone[11]	57	7.57
Propyl acetate[12]	43	7.82
Toluene[13]	91	9.75
Isobutyl acetate[14]	43	10.33
Butyl acetate[15]	43	12.05
Ethylbenzene[16]	91	13.80
m,p-xylene[17]	91	14.14
o-xylene[18]	91	15.23
Diisobutyl ketone[19]	57	18.73
Nitrobenzene[20]	77	24.38

Method detection limits (MDL) were calculated for a 99% confidence level according to US Code of Federal Regulations (US-CFR, 2005) method, corresponding to a signal/noise ratio of 3.

III. RESULTS AND DISCUSSION

A. SPME performed with the 100-PDMS fibre

Table 3 shows calibration curves, regression factors, linearity range and MDL obtained for each compound from TIC and m/z areas when the SPME was carried out with the 100-PDMS fibre. An example of the chromatograms obtained is shown in Figure 1.

From TIC areas, very good regression factors were obtained (r=0.99) in all cases. However, all compound responses showed linearity: up to 4-5 mg/L in the case of TIC areas and up to 3-5 mg/L for m/z curves. Consequently, linearity of some compounds decreased when using regression curves obtained from m/z areas.

On the other hand, m/z quantification method allowed to reduce the detection limits to a ten times lower concentration than TIC for most of the solvents. This higher sensitivity obtained with m/z curves allowed to analyse the most volatile compounds which could not be quantified from TIC (acetone, methyl acetate, methyl ethyl ketone and ethyl acetate).

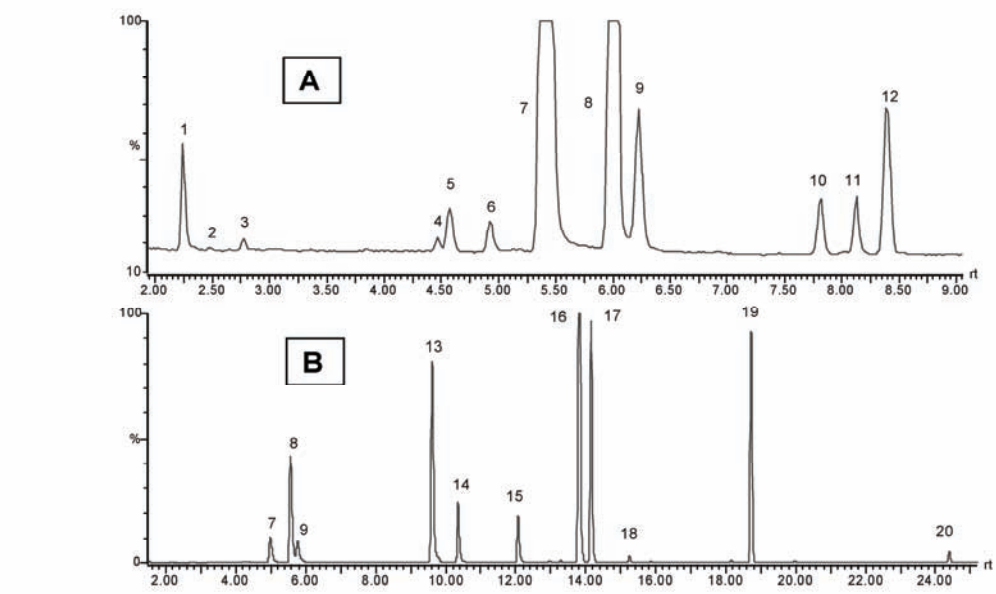

Fig. 1. SPME (100-PDMS)/GC-MS chromatogram of a standard solution of non halogenated solvents at concentration: A=2mg/L and B= 0.1mg/L (compound names according to Table 2).

Table 3. Calibration curves (slope and intercept), regression factors, linearity range and MDL obtained from TIC and m/z areas with the 100-PDMS fibre

Compound		Calibration curve		r	linearity range	MDL
		Slope	Intercept		(mg/L)	(mg/L)
Diethyl ether	TIC	$9.54 \cdot 10^4$	$-3.99 \cdot 10^4$	0.9954	4	0.5
	m/z	$2.53 \cdot 10^4$	$-2.12 \cdot 10^2$	0.9953	5	0.07
Acetone	TIC					2
	m/z	$2.12 \cdot 10^3$	$1.05 \cdot 10^3$	0.9478	5	0.3
Methyl acetate	TIC					2
	m/z	$6.66 \cdot 10^3$	$-1.33 \cdot 10^3$	0.9978	5	0.2
Methyl ethyl ketone	TIC					2
	m/z	$3.51 \cdot 10^3$	$-1.4 \cdot 10^3$	0.9952	4	0.3
Ethyl acetate	TIC					1
	m/z	$5.36 \cdot 10^3$	$-1.03 \cdot 10^3$	0.9996	5	0.2
Tetrahydrofuran	TIC	$2.94 \cdot 10^4$	$1.79 \cdot 10^4$	0.9906	4	0.7
	m/z	$1.04 \cdot 10^4$	$1.60 \cdot 10^3$	0.9951	5	0.1
Cyclohexane	TIC	$3.99 \cdot 10^6$	$5.05 \cdot 10^5$	0.9967	5	0.02
	m/z	$1.08 \cdot 10^6$	$7.49 \cdot 10^4$	0.9938	4	0.003
Benzene	TIC	$1.88 \cdot 10^6$	$3.78 \cdot 10^5$	0.9947	5	0.02
	m/z	$1.03 \cdot 10^6$	$6.69 \cdot 10^4$	0.9935	5	0.002
Isopropyl acetate	TIC	$1.30 \cdot 10^5$	$1.18 \cdot 10^5$	0.9959	5	0.05
	m/z	$1.04 \cdot 10^5$	$2.39 \cdot 10^4$	0.9913	3	0.02
2-pentanone	TIC	$6.77 \cdot 10^4$	-8	0.9907	4	0.3
	m/z	$3.70 \cdot 10^4$	$1.33 \cdot 10^4$	0.9901	4	0.03
3-pentanone	TIC	$5.81 \cdot 10^4$	$1.30 \cdot 10^4$	0.9904	4	0.5
	m/z	$3.55 \cdot 10^4$	$7.82 \cdot 10^3$	0.9961	5	0.02
Propyl acetate	TIC	$1.66 \cdot 10^5$	$7.70 \cdot 10^4$	0.9903	4	0.2
	m/z	$9.33 \cdot 10^4$	$2.58 \cdot 10^4$	0.9867	3	0.02
Toluene	TIC	$7.23 \cdot 10^6$	$6,84 \cdot 10^5$	0.9937	5	0.008
	m/z	$3.29 \cdot 10^6$	$3,01 \cdot 10^5$	0.9943	5	0.0002
Isobutyl acetate	TIC	$5,92 \cdot 10^5$	$2.77 \cdot 10^5$	0.9922	5	0.03
	m/z	$2,10 \cdot 10^5$	$5.71 \cdot 10^4$	0.9824	5	0.003
Butyl acetate	TIC	$7.27 \cdot 10^5$	$3.16 \cdot 10^5$	0.9952	5	0.02
	m/z	$2.25 \cdot 10^5$	$5.57 \cdot 10^4$	0.9814	5	0.005
Ethylbenzene	TIC	$2.26 \cdot 10^7$	$2.32 \cdot 10^6$	0.9902	4	0.002
	m/z	$9.33 \cdot 10^6$	$1.17 \cdot 10^6$	0.9718	3	0.0001
m,p-xylene	TIC	$1.56 \cdot 10^7$	$1.26 \cdot 10^6$	0.9924	4	0.002
	m/z	$5.52 \cdot 10^6$	$5.14 \cdot 10^5$	0.9909	4	0.0003
o-xylene	TIC	$4.04 \cdot 10^5$	$4.91 \cdot 10^4$	0.9933	5	0.05
	m/z	$1.58 \cdot 10^5$	$7.47 \cdot 10^3$	0.9949	5	0.01
Diisobutyl ketone	TIC	$9.61 \cdot 10^6$	$1.29 \cdot 10^6$	0.9914	5	0.002
	m/z	$2.69 \cdot 10^6$	$5.18 \cdot 10^5$	0.9856	5	0.0002
Nitrobenzene	TIC	$4.81 \cdot 10^5$	$7.47 \cdot 10^4$	0.9975	5	0.04
	m/z	$1.73 \cdot 10^5$	$9.13 \cdot 10^2$	0.9975	5	0.01

B. SPME performed with the 85-PA fibre

Calibration curves, regression factors, linearity range and MDL obtained when solvents were collected with the 85-PA fibre are indicated in Table 4.

TIC areas provided very good regression factors (r=0.99) in all cases, similar to the 100-PDMS fibre. The linearity of both responses (TIC and m/z) reached 5 mg/L for all compounds, except for a few specific cases where the linearity decreased for some regression curves obtained from m/z areas.

In a similar way, m/z responses obtained for most of the solvents with the 85-PA fibre allowed to reduce the detection limits about ten times in comparison with the TIC responses.

In this case, 6 volatile compounds could not be quantified from TIC (diethyl ether, acetone, methyl acetate, methyl ethyl ketone, ethyl acetate and tetrahydrofurane). Their concentration had to be calculated from m/z curves.

C. Selection of the SPME fibre

The MDL obtained with the 100-PDMS fibre were better than those corresponding to the 85-PA fibre. The best sensitivity reached with the 100-PDMS fibre could be attributed to the fact that the most volatile compounds (i.e. acetone) were easier adsorbed on the 100-PDMS fibre. Consequently, this fibre reached the saturation at lower concentrations of these compounds in the water samples.

This different behaviour of TIC and m/z responses is illustrated in Fig. 2 and 3.

The wide variety of detector response values could be attributed to the different chemical structures of the selected compounds. In all cases, responses obtained with 100-PDMS fibre were higher than the obtained with 85-PA fibre. For better detectable compounds (Fig. 2), these differences were of the order of 30-40% whereas for compounds represented in Fig. 3, these differences increased until 50-60%.

Table 4. Calibration curves (slope and intercept), regression factors, linearity range and MDL obtained from TIC and m/z areas with the 85-PA fibre

Compound		Calibration curve		r	linearity range	MDL
		Slope	Intercept		(mg/L)	(mg/L)
Diethyl ether	TIC					2
	m/z	$4.15 \cdot 10^{3}$	$-1.99 \cdot 10^{2}$	0.9245	5	0.07
Acetone	TIC					5
	m/z					2
Methyl acetate	TIC					2
	m/z	$3.53 \cdot 10^{3}$	$-4.92 \cdot 10^{2}$	0.9550	5	0.3
Methyl ethyl ketone	TIC					3
	m/z	$1.15 \cdot 10^{3}$	$-2.89 \cdot 10^{2}$	0.9899	5	0.3
Ethyl acetate	TIC					2
	m/z	$1.76 \cdot 10^{3}$	$3.45 \cdot 10^{2}$	0.9981	5	0.2
Tetrahydrofuran	TIC					2
	m/z	$3.45 \cdot 10^{3}$	$-1.22 \cdot 10^{2}$	0.9827	5	0.2
Cyclohexane	TIC	$7.22 \cdot 10^{5}$	$3.69 \cdot 10^{4}$	0.9952	5	0.05
	m/z	$2.06 \cdot 10^{5}$	$1.15 \cdot 10^{3}$	0.9921	5	0.01
Benzene	TIC	$1.30 \cdot 10^{6}$	$2.25 \cdot 10^{5}$	0.9927	5	0.02
	m/z	$6.99 \cdot 10^{5}$	$3.60 \cdot 10^{4}$	0.9945	5	0.003
Isopropyl acetate	TIC	$7.60 \cdot 10^{4}$	$-1.58 \cdot 10^{4}$	0.9932	4	0.3
	m/z	$4.02 \cdot 10^{4}$	$6.67 \cdot 10^{3}$	0.9907	5	0.04
2-pentanone	TIC	$4.83 \cdot 10^{4}$	$-1.28 \cdot 10^{4}$	0.9921	5	0.4
	m/z	$2.26 \cdot 10^{4}$	$1.72 \cdot 10^{3}$	0.9903	5	0.05
3-pentanone	TIC	$3.90 \cdot 10^{4}$	$-1.08 \cdot 10^{4}$	0.9914	5	0.4
	m/z	$2.18 \cdot 10^{4}$	$1.73 \cdot 10^{3}$	0.9948	5	0.03
Propyl acetate	TIC	$9.38 \cdot 10^{4}$	$-1.10 \cdot 10^{4}$	0.9910	5	0.2
	m/z	$4.56 \cdot 10^{4}$	$1.02 \cdot 10^{4}$	0.9896	5	0.03
Toluene	TIC	$4.62 \cdot 10^{6}$	$6.20 \cdot 10^{5}$	0.9919	5	0.009
	m/z	$2.02 \cdot 10^{6}$	$2.61 \cdot 10^{5}$	0.9916	5	0.0005
Isobutyl acetate	TIC	$2.90 \cdot 10^{5}$	$-2.58 \cdot 10^{4}$	0.9959	5	0.1
	m/z	$1.10 \cdot 10^{5}$	$4.63 \cdot 10^{4}$	0.9906	5	0.007
Butyl acetate	TIC	$3.84 \cdot 10^{5}$	$6.07 \cdot 10^{4}$	0.9903	5	0.07
	m/z	$1.17 \cdot 10^{5}$	$4.97 \cdot 10^{4}$	0.9879	5	0.006
Ethylbenzene	TIC	$1.32 \cdot 10^{7}$	$2.35 \cdot 10^{6}$	0.9905	5	0.002
	m/z	$6.81 \cdot 10^{6}$	$8.19 \cdot 10^{5}$	0.9781	3	0.0002
m,p-xylene	TIC	$9.45 \cdot 10^{6}$	$1.26 \cdot 10^{6}$	0.9930	5	0.002
	m/z	$3.33 \cdot 10^{6}$	$4.27 \cdot 10^{5}$	0.9935	5	0.0004
o-xylene	TIC	$2.85 \cdot 10^{5}$	$-5.70 \cdot 10^{4}$	0.9902	5	0.2
	m/z	$9.52 \cdot 10^{4}$	$1.16 \cdot 10^{4}$	0.9932	5	0.01
Diisobutyl ketone	TIC	$3.79 \cdot 10^{6}$	$3.08 \cdot 10^{5}$	0.9972	5	0.002
	m/z	$1.08 \cdot 10^{6}$	$1.30 \cdot 10^{5}$	0.9885	5	0.0003
Nitrobenzene	TIC	$1.65 \cdot 10^{5}$	$-6.45 \cdot 10^{4}$	0.9942	5	0.04
	m/z	$5.08 \cdot 10^{5}$	$4.91 \cdot 10^{3}$	0.9932	4	0.01

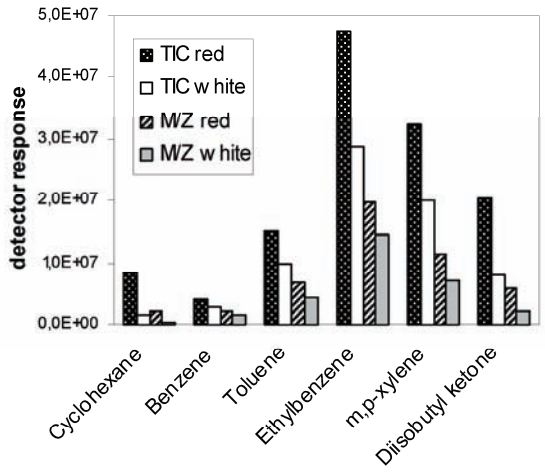

Figure 2. Chromatographic areas (TIC and m/z) corresponding to a 2mg/L solution of the solvents exhibiting the highest detector response (SPME fibres: 100-PDMS and 85-PA)

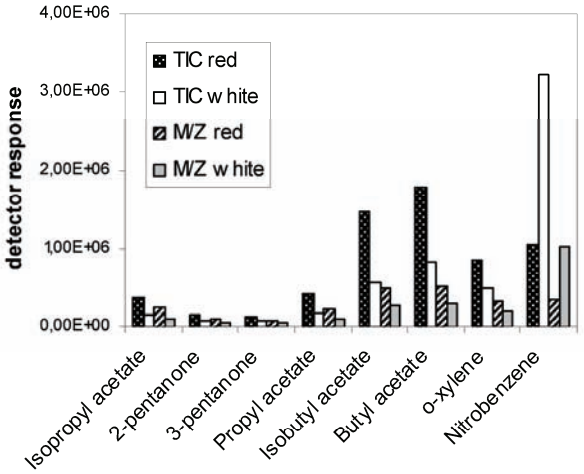

Figure 3. Chromatographic areas (TIC and m/z) corresponding to a 2mg/L solution of the solvents exhibiting the lowest detector response (SPME fibres: 100-PDMS and 85-PA)

D. Comparison of HS and SPME method detection limits

Among the concentration-extraction methods previous to GC-MS analysis —mainly, HS, SPME, CLSA and purge and trap (Golfinopoulos *et al*., 2001; Escalas *et al*., 2003; Huybrechts *et al*., 2000)— Static Headspace is one of the most employed. In fact, optimisation of HS extraction parameters and HS manipulation are easier than SPME. However, HS/GC-MS responses obtained for the selected non halogenated solvents were generally lower than those of the SPME/GC-MS technique (Guadayol *et al*.,2003).

To compare the efficiency of both techniques, method detection limits obtained by SPME (100-PDMS) were compared to those achieved by HS (80ºC, 45 minutes) and submitted to the same chromatographic analysis. These MDL are reported in Table 5.

In general, MDL obtained by the two techniques were similar for most of the solvents, although solvents classified as BTEX (benzene, toluene, ethylbenzene and xylenes) exhibited a much lower MDL when SPME was used. However, the most volatile compounds exhibited the opposite effect: their HS MDL was slightly lower.

For this reason, SPME is a better option when samples are expected to contain BTEX and HS should be chosen when the most volatile solvents are of special interest.

E. SPME application to the analysis of textile wastewaters

The results of the analyses performed on several wastewaters by using the 100-PDMS fibre is shown in Table 6. Samples were collected monthly from three different textile finishing mills, after a treatment in the biological plant.

In the first and second dye houses, solvents classified as BETX were initially detected. In both cases, a higher control of the biological plant was established in order to improve the treatment. Positive results were reached after 1 or 2 months (mills B and A, respectively). At the end of the study, no solvents were detected in any case, after the biological treatment.

None of the studied solvents were detected in treated wastewaters from the third textile company.

IV. CONCLUSIONS

SPME is suitable as a preparative technique for GC-MS. The higher chromatographic responses were obtained

Table 5. MDL obtained from m/z responses with SPME (100-PDMS fibre) and Headsapace (HS)

Compound	MDL (mg/L)	
	100-PDMA fibre	HS
Diethyl ether	0.07	0.1
Acetone	0.3	0.2
Methyl acetate	0.2	0.1
Methyl ethyl ketone	0.3	0.07
Ethyl acetate	0.2	0.05
Tetrahydrofuran	0.1	0.05
Cyclohexane	0.003	0.01
Benzene	0.002	0.006
Isopropyl acetate	0.02	0.03
2-pentanone	0.03	0.03
3-pentanone	0.02	0.03
Propyl acetate	0.02	0.01
Toluene	0.0002	0.002
Isobutyl acetate	0.003	0.008
Butyl acetate	0.005	0.003
Ethylbenzene	0.0001	0.001
m,p-xylene	0.0003	0.002
o-xylene	0.01	0.05
Diisobutyl ketone	0.0002	0.001
Nitrobenzene	0.01	0.03

Table 6. SPME (100-PDMS) and GC-MS analysis of several industrial wastewaters from three different textile finishing factories, taken over three months

Sample	Solvent content	Concentration (mg/L)
A1	o-xylene	0.02
	Toluene	0.004
A2	o-xylene	0.01
A3	none	≤ MDL
B1	Ethylbenzene	0.01
	m,p-xylene	0.04
	o-xylene	0.03
B2	none	≤ MDL
B3	none	≤ MDL
C1	none	≤ MDL
C2	none	≤ MDL
C3	none	≤ MDL

with the 100-PDMS fibre. Hence, the lower MDL corresponded to the 100-PDMS fibre, although it reached the saturation before the 85-PA fibre. In order to obtain a higher sensitivity, the 100-PDMS fibre was selected for the analysis of industrial wastewaters.

In general, HS and SPME have similar MDLs for most of the studied solvents. However, the SPME technique provides a much lower MDL for BTEX, whereas HS allows to obtain a slightly better MDL for the most volatile compounds. In both cases, method detection limits are lower than the levels established in current regulations.

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