

Estimate of the odour potential of industrial wastewater ponds by headspace/SPME/GC/MS

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To study the odorous potential of industrial wastewaters, an analytical method involving Headspace/Solid-Phase Micro Extraction/ Gas Chromatography/Mass Spectrometry (HS/SPME/GC/MS) was developed. The methodology was optimized on real samples by using an experimental design. Among the factors studied, the most influent was the SPME extraction time. The detection limits obtained in GC/MS for various odorous compounds vary from 0.1 to 500 $\mu\text{g.L}^{-1}$ for 2 min extraction. The corresponding gaseous concentrations, calculated from the Henry's law constant, are all below the olfactory perception levels. The methodology was then applied to evaluate the olfactory impact of the sugar industry plant.

1. Introduction

Odorous compounds emitted by agro industrial activities are known to cause annoyance to local residents. Therefore, the classification of the odour sources and the determination of their strengths are key steps in solving an odour problem. In the sugar industry plant studied, odours mainly originate from the ponds of the industrial wastewater treatment plant. The difficulty for such diffusive liquid sources is to perform a convenient sampling of the odorant air above the liquid effluent. One of the most current methods is the use of a dynamic flux chamber (Leyris et al., 2000). This sampling mode is not easy to implement as it requires a clean air source, pumping systems and air flow measurements. Moreover, the measured emission strongly depends on the geometry of the enclosure and on the operating procedures. To simplify the sampling step, an alternative is proposed to estimate the concentrations of the odorous compounds present in the air above the surface. The method consists in sampling and analysing the liquid effluents by Headspace/Solid-Phase Micro Extraction/ Gas Chromatography/Mass Spectrometry (HS/SPME/GC/MS) (Florez et al., 2000; Diaz et al., 2005). From the results obtained in the liquid phase, the concentrations in the gas phase could be deduced from the Henry's law. One of the advantages of the HS/SPME extraction is that it combines, in one single step, liquid/gas extraction of the volatile odorous compounds and their pre-concentration by SPME (Llompert et al., 1999; Snow et al., 2002). Moreover, the method can be fully automated, allowing routine analysis.

This paper deals with the development of the methodology and its application to evaluate the olfactory impact of the sugar industry plant through 2 sampling campaigns.

2. Materials and methods

2.1 Gas chromatography/mass spectrometry

A Varian 3800 gas chromatograph coupled to a 1200Q quadrupole mass spectrometer (MS) (Varian, Les Ulis, France) was used. The PTV 1079 injection port was equipped with a 0.75 mm I.D. liner (dedicated to SPME) and operated at 320°C in splitless mode. Carrier gas was helium with a flow rate of 1 mL.min⁻¹. The chromatographic column was a Varian VF5ms (Varian, Les Ulis, France), 60 m * 0.25 mm * 1 µm. The oven was programmed as follows: 40°C for 4 min, ramped to 190°C at 7°C.min⁻¹ then ramped to 250°C at 10°C.min⁻¹ and maintained at 250°C for 5 min. The transfer line to MS was maintained at 280°C and the ion source at 250°C. Acquisition was performed in electronic impact (EI) mode and started 4.3 min after sample introduction. The mass range used was 20-250 a.m.u. and the acquisition rate was 0.5 scan.s⁻¹.

2.2 Headspace-SPME (HS/SPME)

A Combi-Pal automated sampler (CTC Analytics, Zwingen, Switzerland) was used for HS-SPME sampling. A volume of 2 mL of liquid samples was introduced in 10 mL headspace vials. To obtain liquid/gas equilibrium, elliptic stirring was applied to the sample for a time which will be further optimized. The temperature was fixed at 30°C. HS/SPME was then performed using a PDMS/Carboxen fibre (Supelco, Bellefonte, USA). The extraction time will be studied in the following. SPME fibre was then desorbed in the injection port of the GC at 320°C.

3. Method development

To be representative of the odorous sources considered, development experiments were directly carried out on the liquid effluents of the sugar plant (primary basin water from the washing of beet). Regarding the production period, pH and oxygen demand varied respectively from 5.8 to 6 and from 4400 to 12000 mg.L⁻¹.

Headspace-SPME was considered as follows: liquid/gas equilibrium was attained first, then SPME pre-concentration was carried out in the gas phase, as static headspace is not enough sensitive to detect odorous compounds at their perception levels. The principle of SPME consists of a fused-silica fibre coated with 1 cm length and 10-100 µm thickness of stationary phase (Pawliszyn, 1997; Pawliszyn, 1999). The silica fibre is affixed to the stainless steel plunger in a device that looks like a syringe. The analytes adsorbed on the fibre coating are desorbed in a conventional GC injection port (see § 2.2). Owing to its ease of use, solid-phase micro extraction appears to be an interesting tool for the pre-concentration of the odorous VOCs present in the headspace (Lestremau et al., 2004). A PDMS/Carboxen fibre was selected, as it was shown in previous studies to be the most efficient to extract low molecular weight compounds (Popp and Paschke, 1997; Tuduri et al., 2001; Lestremau et al., 2003; Larroque et al., 2006).

The methodology was optimized on real samples by using an experimental design. Hence, the influencing factors to be studied were defined. Even if they can considerably increase the sensitivity, salting out and pH effects were deliberately not considered to

keep the effluent matrix close to real conditions. In the same purpose, the extraction temperature was fixed at the minimum allowed by the automated sampler (30°C). The sample volume was fixed at 2 mL in a 10 mL vial to satisfy trace detection and to avoid the saturation of the mass detector in case of high VOCs concentrations. Finally, three influencing factors were studied by using a complete factorial design (2³): the sample agitation (200 - 500 rpm), the partitioning time between the liquid phase and headspace (4 - 10 min), and the extraction time on the SPME fibre (2-5 min). The responses considered were the peak areas of five VOCs identified in the pond sample: ethanol, dimethylsulphur, ethyl acetate, 1-butanol and toluene. Whatever the compound, the sample agitation had no significant influence for a confidence level of 95%: a 250 rpm speed was then selected for further experiments. Similarly, none effect of the partitioning time was observed, showing that the liquid/gas equilibrium is achieved, even after 4 min only. Only the SPME extraction time is significant. The best responses were obtained for 5 min extraction, but it was also shown that these conditions can lead to the saturation of the detector for some VOCs. Thus, a compromise was found by implementing a 2 min SPME extraction. The method performances, evaluated for GC/MS analysis in full scan mode, are presented in Table 1. The limits of detection (L.O.D.), calculated for the liquid phase, were extrapolated to the gaseous phase, by using the Henry law constants (Sander, 1999). The detection limits deducted in gas phase are considerably lower than the perception thresholds (Devos, 1990) (Table 1), showing the relevance of the method developed with regards to the odour issue. The repeatability was evaluated as the relative standard deviation (RSD %) for 5 independent analyses of the liquid effluent.

Table 1: Performances of the HS/SPME/GC/MS method developed

	RSD (%)	LOD in liquid sample (µg.L ⁻¹)	LOD in gas phase (µg.m ⁻³)	Perception threshold (µg.m ⁻³)
Ethanol	8.7	539	158	54900
Ethyl Acetate	5.1	6	51	9800
1-butanol	5.0	260	41	1500
Toluene	7.7	0.1	32	5900

4. Characterization of the odour sources of the sugar plant

The methodology was then applied to evaluate the olfactory impact of the sugar industry plant through 2 sampling campaigns, corresponding respectively to the beginning and the end of the sugar production. Three different ponds were studied. The basin "B3" corresponds to the storage of condensates of evaporation from the transformation process for beets. Those effluents are then used for the washing of beets and stored in "B6" (primary decantation basin). The decanted waters are then aerated in basin "B5". The Table 2 presents the concentrations obtained for the different chemical families of odorous compounds identified in the three basins for the two sampling campaigns.

Table 2: Odorous compounds identified and quantified in the wastewater ponds for the two sampling campaigns.

	First campaign (beginning of production)			Second campaign (end of production)		
	B3 ($\mu\text{g.L}^{-1}$)	B6 ($\mu\text{g.L}^{-1}$)	B5 ($\mu\text{g.L}^{-1}$)	B3 ($\mu\text{g.L}^{-1}$)	B6 ($\mu\text{g.L}^{-1}$)	B5 ($\mu\text{g.L}^{-1}$)
Aldehydes	-	382	26008	-	-	4813
Ketones	19,5	63	2232	310	6291	1579
Alcohols	-	1263	2170	12291	639459	239116
Esters	3.7	21	1517	-	7185	921
Volatile fatty acids	-	36	-	-	82	-
Aromatics	3	252	144	3	516	1169
Phenols	-	8	2	-	-	-
Alkanes-	-	-	-	-	4	-
Alcenes-	0,2	1	6	-	-	-
Terpenes	-	-	-	-	-	-
Furanes	0.2	-	-	-	22	-
Sulphurs	0.6	43	134	-	1614	2138
Chlorinated	-	2	11	48	91	87
Amines	2	1	0.1	13	6	-
Total VOCs	29.2	2072	32224	12665	655270	249823

At the beginning of the sugar production, the concentrations of odorous compounds in wastewaters are low. Only the aerated basin (B5) shows high contents, especially for oxygenated VOCs: the aeration process starts again after a long idle period. The second campaign was implemented to the end of the production period. Thus, the high activity level leads to an important increasing of the organic charge of the effluents. The odorous compounds identified are essentially oxygenated ones (97% of the total VOCs for B6), alcohols being obviously preponderant. It can be also pointed out that the concentration of volatile reduced sulphurs, highly malodorous, is particularly high due to fermentation processes. Excepted aldehydes, we observed a decreasing of the concentration of oxygenated compounds between B6 and B5. Therefore, the efficiency of the aerated treatment is about 50% for the oxygenated VOCs.

5. Estimate of the odour potential

The final purpose of this work is to assess the olfactory impact of the liquid sources of the sugar plant studied. It would therefore be interesting to be able to estimate the levels of odorants in the gas phase above the ponds. The concentrations of seven VOCs in the gas phase above the secondary decantation pond were evaluated using the concentrations in the liquid effluent measured by HS-SPME-GC-MS and by using Henry law constants. The outside temperature measured at the time of sampling was 25°C hence, Henry law constants were used at this temperature. The comparison of these calculated concentrations with the olfactory thresholds allows estimating the odour potential of the basin studied. In addition, three grab samples of ambient air (analyzed by SPME/GC/MS) (Larroque et al., 2006b) have been made close to the factory at the same time than the liquid effluent samples. For each sample, monitoring of meteorological parameters (wind direction and speed, temperature, humidity) was implemented.

The results are given in Table 3.

Table 3: Estimate of the odour potential of a decantation basin (C_L : concentration in the liquid effluent; C_G : concentration calculated in the gas phased above the liquid; A, D and T correspond to the 3 samples of ambient air close to the factory).

	Perception threshold (mg.m ⁻³)	C_L (mg.L ⁻¹)	C_G (mg.m ⁻³)	Concentrations measured in ambient air (mg.m ⁻³)		
				A	D	T
Acetaldehyde	0.3	1.1	3.0	-	0.1	-
Ethanol	55.0	16.5	3.9	0.1	0.03	0.06
Acetone	34.7	0.04	0.1	-	-	-
Isopropanol	25.7	0.2	0.1	-	-	-
Ethyl acetate	9.8	0.1	0.8	0.02	-	0.02
1-butanol	1.5	0.1	0.3	-	-	-
Toluene	5.9	0.2	39.0	0.09	0.09	0.1

Except for acetaldehyde and toluene, estimates of the levels of VOCs in the gas phase just above the basin are significantly below the olfactory thresholds. If this estimate is relevant, measures in the ambient air around the site should provide even lower concentrations. This is indeed the case, and some VOCs as acetone, isopropanol and butanol, already low in concentration at the source, are not identified in the receiving environment. This is logical because of the dilution related to the distance of the source and the wind speed.

6. Conclusion

A powerful analytical methodology involving headspace-SPME coupled to GC/MS was developed. The detection limits obtained for various odorous compounds vary from 0.1 to 500 µg.L⁻¹ for 2 min extraction only. Thus, it permits, through a fully automated analysis, to identify and to quantify odorous compounds in complex liquid effluents at their olfactory thresholds. The results allow following the evolution of the different odour sources according to the production activity, and to check the treatment plant efficiency. The odour potential of these liquid sources was also estimated. The relevance of the results was determined by comparing the concentrations calculated in the gas phase from the Henry's law constant with air measurements performed close to the concerned ponds.

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7. References

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