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Solid phase microextraction method for characterizing the organic fraction of an industrial brine stream

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ABSTRACT

The manufacturing process of DOW Chemical Company in Portugal produces a brine stream containing organic contaminants. For recovering the sodium chloride by-product, it is necessary to fully characterize this brine stream. With this purpose, a direct immersion-solid phase microextraction-gas chromatograph (SPME-GC) analytical method was successfully optimized and implemented, being possible to quantify accurately, with reproducibility, the organic fraction at ppb levels. The effects of salt content, extraction time, temperature, and pH were investigated, and the SPME experimental conditions optimized. For the poly(dimethylsyloxane-co-divinylbenzene) fiber utilized, the resulting parameters were: 25% (wt.) of NaCl, 30 min, 20˚C, and pH 11. The fiber desorption was performed at 250˚C for 15 min. The calibration curves of the representative organics of the brine (benzenamine, cyclohexanamine, 2-methylbenzenamine, *N*–cyclohexylcyclohexanamine, cyclohexyl alcohol, nitrobenzene, cyclohexanone, and 4-phenylcyclohexylamine) presented good correlation coefficients ($0.991 \leqslant R^2 \leqslant 0.997$). The detection limits of the method were determined for each species for the optimized analytical conditions; the detection limits vary from 0.21 to 3.22 ppb, respectively for *N*–cyclohexylcyclohexanamine and benzenamine, the, precision ranged from 4.4 to 8.7% RSD and the validation criteria was obeyed for all analytes. The industrial brine stream was then characterized during several days to register the concentration history of contaminants. Independently of the stream composition fluctuations, the SPME methodology developed and optimized in this work was able to assess accurately their concentrations at ppb levels.

Keywords: Solid phase microextraction; Industrial brine; Characterization; Organic; Fraction

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1. Introduction

Brine is a general term to describe salted solutions made directly by dissolving natural or industrial sodium chloride in water or resulting from a chemical process. In this case, brine is released with variable salt concentrations and contaminated with typical process organic or inorganic chemicals. Direct disposal or recycling may be not possible without quality control and/or additional purification.

In the process under question, the brine is a bottom product of a purification column but is still contaminated with typical process organic chemicals at ppb concentration levels that make it not suitable for direct feed to downstream unit operations. The main alkalinity constituents, water, and sodium chloride are variable according to the plant operation conditions but the contaminant species are constant and related to the process chemistry and raw materials used. Table 1 lists the typical organic impurities existent in the brine stream that are being evaluated in this study.

The analytical method implemented at DOW's laboratory for quantifying the organic contaminants is based on a liquid–liquid extraction and subsequent injection in a gas chromatograph (GC). This method has a detection limit of 1 ppm. The liquid–liquid extraction is required because aqueous solutions can damage the capillary column if injected directly. Hence, a new method to detect and quantify these organic contaminants at low concentrations (ppb level) is necessary.

The solid phase microextraction (SPME) is a simple and effective technique used to selectively uptake organics from a sample solution by the coating of a fiber, making possible their concentration by adsorption for subsequent analysis by GC. The SPME technique eliminates the need for solvents or complicated apparatus for concentrating organic species in liquid samples or headspace [1,2]. It is compatible with analyte separation/detection by GC and provides linear results for a wide range of analytes concentration [1]. Typically, SPME is considered complete when the analyte distribution between liquid sample and fiber coating reaches equilibrium. Such condition is described by Eq. (1), where it is assumed that the sample is homogeneous and that no headspace is present in the system:

$$n = \frac{K_{fs} V_f V_0 C_0}{K_{fs} V_f + V_0} \quad (1)$$

where n is the amount of analyte extracted by the coating, K_{fs} is the distribution coefficient, V_f is the fiber coating volume, V_0 is the sample volume, and C_0 is its initial concentration in the sample. In addition, when the sample volume is much higher than that of the fiber coating ($V_0 \gg K_{fs} V_f$), Eq. (1) simplifies to:

$$n = K_{fs} V_f C_0 \quad (2)$$

According to this equation, the amount of analyte in the fiber is directly proportional to the sample concentration, and it is independent of the sample volume [3].

In the 1990s, Noble [4] was one of the firsts in testing the SPME concept. Sections of fused silica and optical fibers—both uncoated and coated with liquid and solid polymeric phases—were immersed into an aqueous solution containing analytes and then inserted in a GC injector. Those early experiments provided very important preliminary data that confirmed the usefulness of this simple approach, since both polar and nonpolar chemical species were extracted rapidly with reproducibility from aqueous solutions. In 1992, the SPME technique experienced a fast growth with the implementation of coating fibers incorporated into microsyringes, resulting in the first SPME device [5]. Over the years, SPME has been used in many fields to detect and/or quantify a great variety of molecules at ppb concentration levels. By selecting an appropriate coating and optimizing the experimental conditions of analysis, the SPME technique can be tuned for a given application. Thus far, SPME has been most broadly

Table 1
List of representative organic components of the brine stream (data source: ChemSpider)

Component	CAS Number	Molecular weight	Boiling point °C
Benzenamine	62-53-3	93.13	183–184
Cyclohexanamine	108-91-8	99.17	133–134
2-Methylbenzenamine	95-53-4	107.17	199–200
N-Cyclohexylcyclohexanamine	101-83-7	181.32	255–256
Cyclohexyl alcohol	108-93-0	100.16	160–161
Nitrobenzene	98-95-3	123.06	210–211
Cyclohexanone	108-94-1	98.15	154–156
4-Phenylcyclohexanamine	19,992-45-1	175.27	277–278

accepted by the food industry, particularly for flavors of coffee, fruit juice, and vegetable oil [6] and fragrances of perfumes [7]. In clinical applications, SPME has been used to monitor anesthetic residues in blood [8], anorectics in urine [9], and drugs in other body fluids [10]. In forensic applications, it has been applied to monitor traces of accelerates in fire debris [11]. The utilization of SPME in olive brines was reported by Navarro et al. [12], although there are no works reported on industrial brine solutions from chemical plants—which is our main objective.

In this essay, the SPME is particularly advantageous for the quantification of organic contaminants of industrial brine. Besides extracting the analytes from the aqueous solution and allowing very low detection limits (ppb level), it also prevents the GC column from being contaminated with salts. On the other hand, the presence of salts in the sampling solution generally diminishes organics solubility in water, increasing SPME efficiency [13].

By controlling the polarity and thickness of the coating fiber, and maintaining consistent sampling time, temperature, pH, ionic strength, sample volume, and stirring velocity, the analytical results can be reproducible even at low concentration limits [14]. According to the literature, the recommended SPME coating material for our solution is poly(dimethylsyloxane-co-divinylbenzene) (PDMS-DVB) [15,16], which was then selected for the present work.

2. Experimental

2.1. Chemicals and materials

Cyclohexanamine, 2-methylbenzenamine, *N*-cyclohexylcyclohexanamine, cyclohexyl alcohol, nitrobenzene, and 4-phenylcyclohexylamine were purchased from Merck (Merck KGaA, Germany, Damstadt). Benzenamine and cyclohexanone were obtained from VWR (VWR International, France, Fontenay) and HACH (HACH Europe S.A/N.V., Belgium, Namur), respectively. Sodium chloride, sodium hydroxide, and hydrochloric acid were purchased from Aldrich (Sigma-Aldrich Chemie GmbH, Switzerland). All chemicals were of analytical grade. Brine was from DOW, Portugal. The SPME fiber and manual holder assembly were acquired from Supelco (Bellefonte, PA, USA). Non-ionized water, conductivity $< 0.1\,\mu S\,cm^{-1}$, was used.

2.2. Apparatus

Gas chromatography was carried out with Hewlett-Packard 5890 series® system equipped with a split/splitless injector (split ratio 1:70), a flame ionization detector, and a data acquisition software, Thermo Atlas®. Compounds were separated on a 30 m × 0.53 mm I.D., 5.0 μm film thickness CP-SIL 8 CB fused silica capillary column (Agilent Technologies, Palo Alto, CA, USA). The separation was performed from 85 to 270°C ramped at $10^{\circ}C\,min^{-1}$ with helium as a carrier gas at a flow rate of $15\,mL\,min^{-1}$. The injector and detector temperatures were both maintained at 250°C. The detector flow rates were set to $450\,mL\,min^{-1}$ for air, $10\,mL\,min^{-1}$ helium (make up gas), and $40\,mL\,min^{-1}$ for nitrogen.

3. Results and discussion

3.1. Determination of solid phase microextraction optimized conditions

The SPME technique takes advantage of the affinity of fiber coating to the solutes in solution. The amount of analytes extracted depends on the extraction time, temperature, pH, ionic strength, and analytes concentrations in the sample. In order to ensure accuracy and precision, consistency in sampling time and other sampling parameters are more important than full equilibration [17]. The sorption isothermal curves for aromatic amines are linear at ppb concentration levels, so the effect of multicomponent sorption interactions should be negligible [18].

In the following, it is described the experimental procedure adopted, particularly the variables fixed along all essays. The optimization of the ionic strength, temperature, pH, and extraction time of SPME are presented and discussed below, in individual subsections for clarity.

A standard aqueous solution containing 1 ppm of each component listed in Table 1 was prepared. The fiber coated with PDMS-DVB (65 μm film thickness) was conditioned in the GC injection port at 250°C for 30 min before use. The fiber (i.e. the PDMS-DVB coating) was immersed 4 cm into the sample contained in a 10 mL glass vial at fixed temperature and under a stirring velocity of 700 rpm for a given period of time; preliminary tests indicated that headspace SPME technique originates clearly worst results. Other sorption conditions were set and maintained constant: pH and the weight percentage (%wt.) of sodium chloride (to fix the ionic strength). The coating was manually inserted in the GC port and the analytes were desorbed at 250°C for 15 min. The solutes exit the column essentially according to their boiling point. All peaks were well defined and amenable for standard GC analysis at ppb concentrations levels. Whenever needed, the PDMS-DVB coating fiber was cleaned by immersing it in a

stirred 10% (vol.) methanol/water solution for 30 min at room temperature.

3.2. Effect of ionic strength

A salting-out effect is often used to improve the extraction efficiency of polar species. With this purpose, samples with sodium chloride contents of 0, 10, and 25% (wt.) were investigated. Other sorption conditions were kept constant: pH 7, temperature at 20˚C, and extraction time of 10 min.

For many organic analytes, their aqueous solubility decreases with increasing ionic strength and their extraction efficiencies improve [15,16]. Fig. 1 shows that this statement is true except for 4-phenylcyclohexylamine, for which the amount extracted—proportional to peak area—decreases as salt concentration increases. The extraction efficiency of 4-phenylcyclohexylamine is hampered at higher salt concentrations, but its quantification is not penalized at all. Hence, a salt concentration of 25% (wt.) was then selected for further experimentations—since it favors the remaining compounds detection. Additionally, taking into account that the salinity of brine is around 10%, it is necessary to have a superior set point value for its accurate analysis.

3.3. Effect of extraction temperature

By increasing the temperature, the sorption equilibrium is reached faster, though the analyte affinity to the fiber coating decreases. The effect of the extraction temperature was investigated in this work by selecting three temperature levels: 20, 45, and 70˚C. The other sorption parameters were kept constant: 25% (wt.) of salt, pH 7, and extraction time of 10 min.

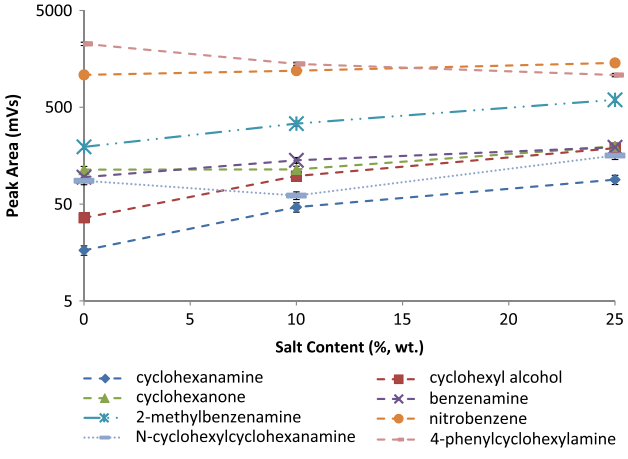

Fig. 1. Effect of the salt content upon the extracted amounts of each solute (proportional to peak area) using semi-log plots. Samples: 1 ppm of each species, pH 7, 20˚C, extraction time = 10 min.

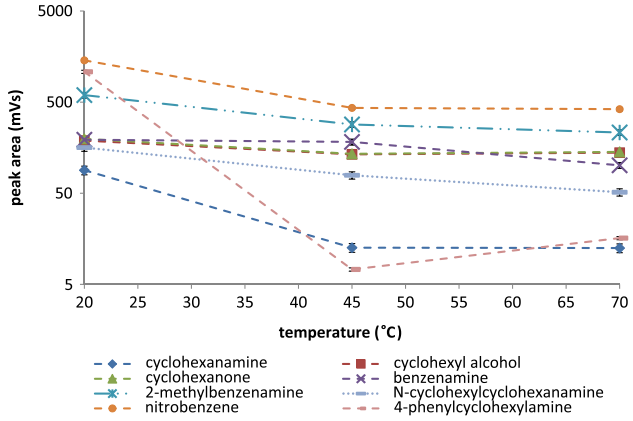

Fig. 2. Effect of the temperature upon the extracted amounts of each solute (proportional to peak area) using semi-log plots. Samples: 1 ppm of each species, 25% (wt.) of NaCl, pH 7, extraction time = 10 min.

As can be seen in Fig. 2, the amount of analytes sorbed on the fiber coating decays substantially as temperature increases. Accordingly, further experiments were then performed at 20˚C.

3.4. Effect of solution pH

Monocyclic aromatic amines, which are weak bases, must be predominantly in the non-ionized state for extraction. Subsequently, the pH of sampling solutions was adjusted by adding a strong base, sodium hydroxide (NaOH, 1 M) or a strong acid, hydrochloric acid (HCl, 1 M). Values pH 2, 7, and 11 were investigated (the fiber is limited to a pH range between 2 and 11). Other sorption parameters were kept constant: salt concentration of 25% (wt.), temperature of 20˚C, and extraction time of 10 min. As can be seen in Fig. 3, for all species, the amount of organics extracted by the fiber coating increases with increasing alkalinity of sampling solutions with the exception of cyclohexanone in pH range 2–7. Particularly for benzenamine, cyclohexanamine, 2-methylbenzenamine and *N*-cyclohexylcyclohexanamine, the extraction is highly ineffective under acidic conditions (pH 2) and is found to be at the maximum at pH 11. This experimental observation was also reported by other authors for aromatic amines [15,19], who concluded that the extraction efficiency of aromatics is higher for basic conditions. Hence, pH 11 was selected for further experimentation.

3.5. Effect of extraction time

According to Raghani [20] and Lin et al. [21] some components can take 10 min to attain the sorption equilibrium and others can take even longer times

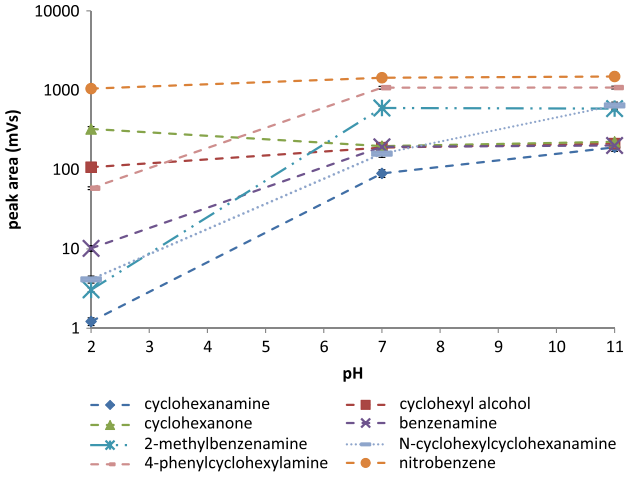

Fig. 3. Effect of the pH upon the extracted amounts of each solute (proportional to peak area) using semi-log plots. Samples: 1 ppm of each species, 25% (wt.) of NaCl, 20°C, extraction time = 10 min.

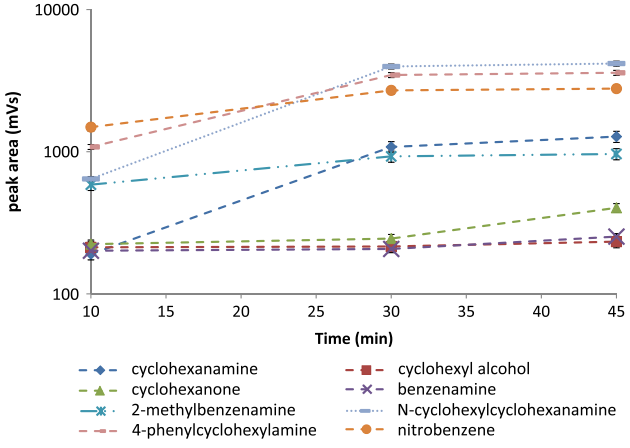

Fig. 4. Effect of the extraction time upon the extracted amounts of each solute (proportional to peak area) using semi-log plots. Samples: 1 ppm of each species, 25% (wt.) of NaCl, 20°C, pH 7.

depending on the molecular size and chemical affinity to the fiber coating, among other factors. The PDMS-DVB fiber was immersed in 10 mL of the standard solution (1 ppm of every component), with magnetic stirring (700 rpm) at 20°C during 10, 30, and 45 min. Other sorption parameters were kept constant: 25% (wt.) of NaCl and pH 7. Fig. 4 shows that lower molecular weight species such as benzenamine, cyclohexanamine, 2-methylbenzenamine, cyclohexyl alcohol, and cyclohexanone reach the equilibrium after ca. 10 min, but higher molecular weight molecules, such as *N*-cyclohexylcyclohexanamine, nitrobenzene, and 4-phenylcyclohexylamine required around 30 min. Accordingly, in this work, this has been selected as the extraction time. Additional experiments with brine samples confirmed that 30 min are adequate for the extraction of the analytes considered.

3.6. Calibration curves

The calibration was performed at the optimized SPME extraction conditions obtained above: 25% (wt.) of salt content, 20°C, pH 11, 30 min extraction time (see Table 2). Four external standard aqueous solutions containing 1000, 500, 100, 50 ppb of each of the eight species were prepared. The pH and salt content of all these solutions were adjusted to 11 and 25% (wt.) of NaCl, respectively. The analysis was carried out for each standard solution. The PDMS-DVB fiber was immersed in 10 mL of the stirred sample solution during 30 min at 20°C. Each standard was replicated five times. The calibration curves for each species were determined with good correlation coefficients, $0.991 \leqslant R^2 \leqslant 0.997$. To adjust the calibration curves to Eq. (2), the zero regression was forced. The reproducibility was assessed for each species based on the relative standard deviation, RSD (%), and values between 0.9 and 10.9% were calculated, which indicates a good reproducibility of the analytical method.

3.7. Detection limits, precision, and method validation

Detection limits, precision, and method validation were performed for the eight species based on eight replicate analyses of an industrial brine sample and using the optimum analytical conditions previously obtained. This brine sample was spiked with a known amount of the eight species—see Table 3. The spiked concentration was selected to originate approximately the same signal in the GC. The detection limits were made equal to the 99% confidence interval assuming Student's *t* distribution of eight spiked replicate samples [15] and the precision was made equal to the relative standard deviation of the replicate analyses

Table 2
SPME optimized extraction conditions

Parameter	Value
Sample volume (mL)	10
Stirring velocity (rpm)	700
Extraction time (min)	30
Temperature (°C)	20
pH	11
Salt content (%, wt.)	25
Desorption time (min)	15

Table 3
Detection limits of the method (DL), precision (RSD, %), and method validation for the organic species considered (the concentration difference between the spiked and the pristine brine samples must be equal to the spiked concentration plus/minus the detection limit)

Species	Brine sample		Detection limits determination		Method validation			
	Mean (ppb)	RSD (%)	Spiked concentration (ppb)	DL (ppb)	Spiked concentration (ppb)	Mean (ppb)	RSD (%)	Criteria Obeyed/not obeyed
Benzenamine	311	7.1	20	3.22	35	349	6.9	✓
Cyclohexanamine	21	6.5	15	1.89	20	42.7	6.2	✓
2-methylbenzenamine	5.2	5.9	5	0.41	4	9.4	5.7	✓
N-cyclohexylcyclohexanamine	26	4.7	5	0.21	2	28.1	4.4	✓
Cyclohexyl alcohol	252	6.9	15	2.18	20	274	6.8	✓
Nitrobenzene	1.9	5.5	5	0.37	4	6.0	5.3	✓
Cyclohexanone	33	8.9	15	1.93	20	54.3	8.7	✓
4-phenylcyclohexylamine	1.4	5.1	5	0.79	4	5.5	4.8	✓

(RSD,%). The method was validated based on the analytical results of the pristine brine sample and the sample spiked at concentrations approximately 10 times higher than the detection limits [15]; the concentration difference between the pristine brine sample and the spiked one must be equal to the amount spiked plus/minus the detection limit—Table 3.

The detection limits range from 0.21 to 3.22 ppb, corresponding respectively to *N*-cyclohexylcyclohexanamine and benzenamine analytes, precision values ranged from 4.4 to 8.7% RSD and the validation criteria was obeyed for all analytes.

3.8. Characterization of a brine stream

Once a day, during 12 days, a sample was collected from the brine stream and submitted to the following procedure: (a) the salt concentration of the sample was determined by potentiometric titration with silver nitrate ($AgNO_3$) [22]. In general, the salt content was between 9 and 12% (wt.) implying its adjustment to 25% (wt.); (b) the pH was ca. 13.5, implying to be adjusted to 11 using HCl solution 1 M; (c) the SPME extraction was performed according to the optimized conditions of Table 2; (d) the loaded PDMS-DVB fiber coating was inserted in the GC port during 15 min at 250 °C, for desorption. Each sample was analyzed twice; and (e) at the end of each day, the SPME fiber was cleaned as described above in the introduction of Section 3. The daily history of the brine organic fraction assessed during 12 days is plotted in Fig. 5. The variations observed reflect the product grade being produced by the plant. The average composition of the stream during the

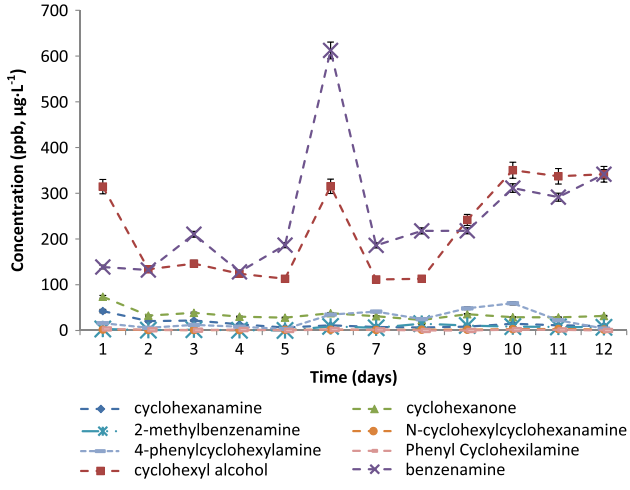

Fig. 5. Organic fraction concentrations history of the process brine stream of DOW.

Table 4
Characterization of the process brine stream during 12 days (see Fig 5)

Species	Average concentration ± SD ($\mu g\,L^{-1}$)
Benzenamine	225 ± 79
Cyclohexanamine	15 ± 10
2-Methylbenzenamine	6 ± 2
N-Cyclohexylcyclohexanamine	24 ± 19
Cyclohexyl alcohol	212 ± 101
Nitrobenzene	2 ± 1
Cyclohexanone	35 ± 13
4-Phenylcyclohexylamine	2 ± 1

sampling period is plotted in Table 4. Benzenamine and cyclohexyl alcohol are the species with higher concentration (225 ± 79 and 212 ± 101 $\mu g\,L^{-1}$, respectively), while nitrobenzene and 4-phenylcyclohexylamine have residual concentrations of 2 ± 1 $\mu g\,L^{-1}$. The analytical procedure developed and optimized in this work allowed an efficient and reliable analysis of the organics present in the process brine stream at ppb concentration levels.

4. Conclusions

A direct immersion-SPME-GC method using PDMS-DVB fiber was implemented and optimized for quantifying the organic fraction of a brine by-product stream from DOW Chemical's Portugal plant at ppb levels. The characterization of this stream is essential for the development of a sodium chloride recovery process. The optimized conditions of the extraction step are pH 11, 25% (wt.) of NaCl (a measure of ionic strength), extraction time of 30 min, and a temperature of 20˚C. The calibration curves obtained showed good correlation coefficients ($0.991 \leqslant R^2 \leqslant 0.997$). The experimental replication of the method indicated a good reproducibility ($0.9 \leqslant \text{RSD}\ (\%) \leqslant 10.9\%$). The detection limits were determined for each species and ranged between 0.21 and 3.22 ppb, respectively for *N*–cyclohexylcyclohexanamine and benzenamine; precision values ranged from 4.4 to 8.7% RSD, respectively for 4-phenylcyclohexylamine and cyclohexanone, and the validation criteria was obeyed for all analytes.

The concentration history of the selected organic compounds in the process brine stream was measured during 12 days. The organics concentration exhibited large variations with the product grade that was being produced in the industrial plant. Benzenamine and cyclohexyl alcohol showed the highest concentrations (225 ± 79 and 212 ± 101 $\mu g\,L^{-1}$, respectively) while nitrobenzene and 4-phenylcyclohexylamine had the lowest ones (2 ± 1 $\mu g\,L^{-1}$ for both species). Whatever the case, and independently of the brine stream fluctuations, the SPME methodology developed and optimized in this work was able to assess their concentrations accurately.

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List of symbols

n — the amount of analyte extracted into the coating
K_{fs} — the distribution coefficient
V_f — the fiber coating volume
V_0 — the sample volume
C_0 — initial concentration of the analyte in the sample

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