Development of a Headspace-Gas Chromatography-Mass Spectrometry Method Based on Matrix-Matched Calibration for Evaluating VOC Content, Characterization, Source, and Risk in RO Membrane

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Abstract

Analytical methods have been developed to determine volatile organic compounds (VOCs) in reverse osmosis (RO) membrane using headspace with gas chromatographic mass spectrometry (HS-GC/MS). The operating parameters, including incubation temperature, incubation time and the choice of matrix modifier, were investigated. The existence of matrix effect was checked and the VOC-free RO membrane was selected as the best material for developing matrix-matched calibration curve. At optimum operating conditions, the established method performed good linearity ($R > 0.996$), repeatability ($< 9.5\%$), VOC recoveries (84.7%–123%) and detection limits (3.44–748 $\mu\text{g/kg}$). The method was applied to determining thirty-seven common VOCs for RO membrane and toluene and N,N-dimethylformamide were the most abundant VOCs in measured samples, with average contents of 90 087 $\mu\text{g/kg}$ and 249 957 $\mu\text{g/kg}$ respectively. Besides, compounds including acetone, dichloromethane, hexane, chloroform, 1,2-dichloroethane, benzene, chlorobenzene, ethylbenzene, xylene, styrene were also found with content between N.D.–112 419 $\mu\text{g/kg}$ in detection rate between 40%–100%. The analysis of VOC distribution showed the solvents used during the production of the RO membrane were the main source of VOCs in commercial RO membrane. Of these VOCs, dichloromethane, chloroform, 1,2-dichloroethane, and toluene were hardly removed by pre-washing. The relationship between the content of VOCs in RO membrane and their corresponding concentration in filtrated water showed highly positive correlation and the safety limit values for the four compounds were evaluated as 2.6×10^2 – 3.8×10^5 $\mu\text{g/kg}$, but more accurate and completed guideline values should be formulated to guarantee the RO membrane quality.

1. Introduction

Water pollution in surface water and underground water is becoming serious in worldwide nowadays. Heavy metals and organic compounds are the most focused pollutants in water sources and for decades, many water treatment technologies, including biological process, electrochemistry, chemical reduction, and physico-chemical method, are used in water disposal (Hou et al., 2018; Hou et al., 2015; Ren et al., 2016; Sharma and Bhattacharya, 2016). Of these technologies, the reverse osmosis (RO) membrane technology has been extensively employed in urban households and poverty-stricken regions all over the world, because it is able to synchronously remove contaminants, including heavy metals, organic compounds, and bacteria (Sharma and Bhattacharya, 2016).

The primary concept of RO was started by Loeb and Sourirajan in the 1960s through the introduction of asymmetric cellulose acetate membrane, but commercial application in this field thrived with the development of thin film composite (TFC) RO membrane owing to its salt rejection, resistance to pressure compaction, and wide operating temperature range and pH range (Kang and Cao, 2012; Li and Wang, 2010; Liu et al., 2011). For decades, studies have been intensively focused on the development of the RO membranes by using novel materials and methods for synthesis to increase the RO membrane's performance in terms of high water flux, long lifetime, and resistance to chlorine and membrane fouling (Shi et al., 2017; Wei et al., 2010; Zhang et al., 2013). Notably, many volatile organic compounds (VOCs), such as toluene (Tol), hexane (Hex), and N,N-dimethylformamide (DMF), are widely used as solvents during the synthesis and modification of the RO membrane (Emadzadeh et al., 2015; Guillen et al., 2011; Rana et al., 2015). For this reason, removing the residual organic compounds during the production process of RO membrane is an essential step which is performed by squeezing using a roll rubber, drying at ambient temperature $\sim 90^\circ\text{C}$, and washing by pure water (Liu et al., 2014; Yan et al., 2016; Zhao et al., 2017). However, before the use, pre-washing for a certain time is still a required step in RO operation specification to ensure the quality of effluent water. Nevertheless, residual organic contamination in commercial RO membrane is also a crucial problem even if few studies have been published about it.

Countries in the worldwide have formulated standards to ensure the quality of the materials in contact with water. National Sanitation Foundation of United States (NSF) has established a series of standards for evaluating the materials and units for drinking water treatment, and these criteria have also been quoted as the American National Standard (NSF/ANSI, 2015; 2017; 2018). Of these criteria, NSF-58 Reverse Osmosis – Drinking Water Treatment Systems was the main reference used for the evaluation of the health effects of RO membrane, and it introduced a classical method referred to as the extraction testing. According to this method, samples were completely filled with exposure water which contained 50 ± 5 mg/L of total dissolved solids and 0.5 ± 0.05 mg/L of free available chlorine and have a pH of 6.75 ± 0.25 , and maintained for 24 h at an ambient temperature of $23 \pm 2^\circ\text{C}$. At least 2 L of exposure water shall be collected for analysis and the above process shall be repeated to give a total of three times. Similarly, State Bureau of Technical Supervision of China also published criteria in accordance with NSF's method to ensure the health security of water-contact materials used in drinking water treatment and toluene (Tol), dichloromethane (DCM) and trichloromethane (TCM) were selected as the candidates in the testing of RO membrane (SBTS, 1998). However, the shortcomings of this method are that it required plenty of time for preprocessing, and the products which were certificated by NSF standards were possible to cause problems in practice since there existed deviations between extraction testing and the actual use (Heim and Dietrich, 2007; Triantafyllidou et al., 2012). In addition, common solvents, such as DMF and Hex, are not limited by above criteria. Therefore, developing a fast and comprehensive method for the determination of the residual organic components in RO membranes is significant to ensure their sanitary safety for household use.

In this investigation, we developed an analytical method for the determination of VOCs in RO membrane using headspace-gas chromatography-mass spectrometry (HS-GC/MS). The influence of parameters, including matrix modifier selection, incubation time and temperature, were optimized. The effect of the existence of matrix effect was also studied. The method developed in this paper was used to analyze the VOC content of commercial RO membranes, and sources of various VOCs were also discussed. In addition, risk assessment conducted by evaluating the relationship between specific VOC content in RO membrane and their concentration in effluent water was also investigated. The results obtained in this study could provide the foundation for future contamination analysis and development of the RO membrane.

2. Experimental

2.1 Chemicals and standard solutions

Methanol and acetonitrile were HPLC grade and purchased from Fisher Chemical, China. VOC standard solutions, nylon membrane and mixed cellulose ester membrane were obtained from ANPEL Scientific Instrument Co., Ltd., China. Deionized water was obtained with a Milli-Q purification system. A stock solution

of the VOCs was prepared in methanol and stored in a refrigerator at 4°C for no more than 12 h.

2.2 RO membrane samples

To estimate the VOC content in RO membrane, various samples purchased from different manufacturers were used in the experiments (RO1–RO10). Before the experiments, each sample of RO membrane was dismantled into three parts, namely, the outer packing gummed paper, RO membrane, and gauze element. The dismantled RO membranes were stored in sealed valve bags away from light and analyzed within 2 h. Before analysis, RO membrane samples were rapidly cut down to a size of 5 cm×2 cm, and the samples at 0.2 g were placed into a headspace bottle that was contained by a certain matrix modifier (if have). Afterward, the headspace bottles were closed with an aluminum seal and waited for analysis. The incubation time for equaling samples was in the range of 15–180 min, and the oven temperature was in the range 45°C–140°C. The injection volume was 1000 µL. Calibration curves were constructed by plotting the peak areas against the content of each analyte, and then, the contents of VOCs in RO membranes were calculated according to the following formula:

$$\rho = \frac{c}{m \times (100 - w)} \times 100 \quad (1)$$

where ρ is the content of VOCs in RO membrane (µg/kg), and c is the mass of the measured individual VOCs by HS-GC/MS (ng). m is the sample mass (g), and w is the moisture content (%) of each sample.

2.3 Pre-washing of RO membrane

A RO water purifier (Fig. 1) without other purification crafts was used to investigate the practical effect of residual VOCs in RO membrane on purified water quality. The RO membrane used was in the same batch as the above experiments. Deionized water without VOC background was pumped into the experimental RO membrane at speed of 0.5 L/min, and the VOC concentration in effluent water was determined within 24 h.

2.4 Instrument and sample analysis

An automated headspace instrumentation (Dani, HSS 86.50, U.S.A) set at certain temperature (45°C–140°C) was used for the pretreatment of the samples. The loop (1000 µL) and line transmission line temperatures were 150°C and 170°C, respectively. The VOC content of the RO membrane was analyzed in a gas chromatograph system (Shimadzu, 2010 plus, Japan) equipped with a mass detector (Shimadzu, QP 2020, Japan). A 624MS chromatographic column (30 m × 0.25 mm × 1.4 µm, Shimadzu, Japan) was used to separate individual VOCs. Helium (99.999%) was used as carrier gas at 1.17 mL/min, and the injector was operated in a split of 1:5 ratio. The injector temperature was 230°C, and the results were obtained using the following program: the column temperature was initially at 40°C for 5 min after injection and then increased at 20°C/min to 200°C. For mass spectrometry, ionization was carried out by electronic impact (EI) with a voltage of 70 eV and full scan mode in the m/z range of 35–400. The ion and transference temperatures were set at 230°C and 200°C, respectively. Analyte retention times and the ions for analysis in HS-GC/MS are shown in Table S1.

The VOC concentration in effluent water was measured by a standard method under the instrumental conditions mentioned above (MEP, 2016). The DMF's concentration in water was detected by high-performance liquid chromatography (Shimadzu, Japan) with an InertSustain C18 column (150 mm × 4.6 mm, 5 µm) and UV detection at 198 nm. The mobile phase was acetonitrile and water (5: 95 V/V%) with a flow rate of 0.8 mL/min. The column oven was set at 35°C. After filtration through a 0.22 µm filter membrane, the DMF in samples was measured with direct injection method.

3. Results And Discussion

3.1 Experimental conditions optimization

To accurately analyze the VOCs in RO membrane, investigating the effects of various experimental conditions was necessary. A preliminary screening of VOCs showed that DCM, Tol, DMF, chlorobenzene (PhCl), and xylene (Xyl) were abundant in the RO membrane (Fig. 2). Thus, they were employed to optimize the operation parameters of the headspace. In this study, the matrix modifier, incubation temperature, and incubation time were investigated by comparing the variations in GC/MS spectrum peak areas under various experimental conditions.

The matrix modifier aiming at improving the recovery rates or the signal abundance was typically used for the analysis of VOCs in aqueous/solid phase as it could decrease or eliminate the effect from the studied matrix without altering the natural levels of the analyte of the interest (Cavalcante et al., 2010). In particular, saturated NaCl solution or phosphoric–NaCl solution were extensively used in standard methods widely (MEP, 2016; USEPA, 1996). As we known, headspace formation methodologies contribute to signal intensity, thus the addition of a salt modifier in sample system that is not saline favors would increase the signal intensity. However, Cavlcante et al. observed the VOCs determination was not dependent on salinity and pH change (Cavalcante et al., 2010), and the similar results was also obtained by Menendez et al. when using NaCl saturation for sample preparation (Menendez et al., 2000). On the other hand, direct analysis of VOCs in samples without the addition of any modifier has been practiced in material testing owing to its convenience and high sensitivity (Hwang et al., 2019; Lim et al., 2014; Seo and Shin, 2010).

In these experiments, the variations in GC/MS spectrum peak areas under various experimental conditions are shown in Fig. 3. It can be seen that the sample used did contain VOCs and Tol showed the highest peak areas among the five VOCs. The peak areas obtained by direct analysis were apparently higher than those with the addition of matrix modifier (Fig. 3A), especially for Tol, DMF, and Xyl. The reason for this could be partly because these VOCs are both difficult to escape into aqueous phase from samples and into gas phase from aqueous solution. Thus, the modifier used in experiments decreased the gas phase concentration of the targeted compounds.

Incubation temperature often plays an important role on headspace analysis because the higher the incubation temperature is, the higher the diffusion rate for analytes from the sample to the headspace is. As shown in Fig. 3B, the area peak for the five VOCs slowly increased with increasing incubation temperatures from 45°C to 80°C, but then dramatically increased when the incubation temperature was increased from 80°C to 140°C. However, the higher incubation temperatures requires more energy consumption and lead to a higher interior pressure and more water vapor in the head space bottle. In this study, when the incubation temperature was beyond 100°C, the risk of top lid bursting greatly increased.

Incubation time is also an important parameter that affects the sensitivity on the measurement of the VOCs in the samples. Figure 3C shows that the VOC peak areas sharply increased with the 15–60 min equilibrium time and then slowly decreased with 60–180 min equilibrium time. The result illustrated the VOCs, even with the low boiling point, required a relatively long time for release. Thus, the optimal experiment conditions for headspace were determined as follows: headspace equilibrium without matrix modifier, equilibrium temperature of 100°C, and equilibrium time of 60 min.

3.2 Evaluation of the matrix effect and method validation

Matrix effect is often essential to the influent of the component of the aqueous/solid matrix in the GC/MS determination, and the ways to combat matrix effects in GC–MS have been extensively studied (Cavalcante et al., 2010; Ferrer et al., 2011; Garcia Pinto et al., 2011). However, each of the approaches has advantages and disadvantages in certain aspects and among the approaches, matrix-matched calibration is widely used due to its wide applicability and economic benefits (Kwon et al., 2012).

In this study, in order to explore the matrix effect, several matrixes including Nylon Membrane, Mixed Cellulose Ester Membrane, and RO Membrane (samples RO1) were selected as the matched matrixes. For the preparation of calibration curve, all matrix materials were baked in 105°C for a certain period for the preparation of VOC-free matrix. The prepared matrix with mass at 0.20 g was filled into the headspace bottle, and 1 µL of VOC standard solution at concentration 100–2000 ng/µL (2 000–20 000 and 50 000–500 000 ng/µL for Tol and DMF, respectively) was injected rapidly into the matrix materials. Then, the top lid of the headspace bottle was soon compressed by a specific tool. The calibration curve was established with peak areas of quantitative ions and the mass of the added VOCs using external standard method.

Correlation coefficients (*r*), relative standard deviations (RSDs), recoveries, limits of detection (LODs), and limits of quantitation (LOQs) were employed to verify the validation of the proposed method under optimized headspace condition. Table 1 gives an overview of calibrations for all substances analyzed by means of the matrix-matched method (only showed the VOCs detected in testing samples). All of the selected matched matrixes showed good linearity in the concentration range of 100–2 000 ng or 2 000–20 000 ng or 50 000–500 000 ng with the correlation coefficients (*r*) ranging from 0.9960 to 1.0000. However, the slopes of the curve developed by different matrix showed significant differences. For instances, the slopes obtained were in the range 167 to 372 for TCM and 5.83 to 96.7 for DMF, demonstrating that the matrix effect had a great influence on the determination of VOCs in RO membranes (Garcia Pinto et al., 2011).

For recoveries, three levels of the standard adding (5 000, 10 000, 20 000 ng for Tol and 50 000, 200 000, and 500 000 ng for DMF and 100, 500, 2000 ng for others) were used to verify the method validation. It can be seen that by matrix-matched calibration, most targeted compounds (except DMF) showed good results of 70–130% (Table 1), but the calibration developed without adding matrix (empty gas) showed higher slope and insufficient recovery rate for most of these compounds, indicating the absorption of VOCs in matrix decreased their concentration in vapor phase. It is worthily noting that DMF showed very poor recoveries, except when the VOC-free RO membrane used as the matrix material. Afterwards, the VOC-free matrix-matched calibration was used for evaluating the reproducibility of different VOCs and the RSD values of the analytic VOCs were all below 9.5% at above three content levels (*n* = 6), indicating the proposed method had good reproducibility.

Limits of detections (LODs) and quantitation (LOQs) were measured by means of the signal to noise ratio. Noise was determined experimentally from the blank samples and LOD was defined as S/N of 3, LOQ as S/N of 10 (Trefz et al., 2012). Table 2 shows the LODs and LOQs, as well as the corresponding retention time, quantitative ions, qualitative ions, and calibration curve for various VOCs. Most of the compounds presented LODs of no more than 15 µg/kg and LQDs of no more than 48 µg/kg. However, compared with these compounds, DMF (a universal solvent) showed a much higher LOD (748 µg/kg) and LQD (2493 µg/kg) mainly due to its high boiling point and strong absorption on matrix materials.

3.3 VOC distribution and VOC sources

VOCs in 10 RO membrane samples from different manufacturers were determined by the developed method. Table 3 illustrated the analysis results of RO membrane samples. Clearly, all experimental samples contained at least four VOCs. The total amount of VOCs (Σ VOCs) in various RO membrane samples varied from 107 309 to 1 189 847 µg/kg dry weight with a mean concentration of 371 574 µg/kg.

Among the screened 37 VOCs (Table S1), only DMK, DCM, Hex, TCM, DCA, benzene (PhH), Tol, DMF, PhCl, ethylbenzene, Xyl, and styrene were detected. The detection rate of each VOCs in RO membrane was in the following order: DMF (100%) = Tol (100%) = Xyl (100%) > ethylbenzene (90%) > PhCl (80%) > DMK (70%) = Hex (70%) = PhH (70%) = styrene (70%) > TCM (60%) = DCA (60%) > DCM (40%). This order showed that these VOCs were used in RO membrane production at different degrees. Tol and DMF were relatively abundant with mean contents of 90 087 and 249 957 µg/kg, representing 24.2% and 67.3% of mean Σ VOCs, respectively. For individual sample, the contents of Tol and DMF were also dramatically higher than those of other VOCs, and their content were respectively accounting for 5.80–60.0% and 27.9–89.3% of Σ VOCs over the tested samples. As the VOCs should originate from the production and processing of RO membrane and the VOC content, such as DMK, DCM and TCM, showed discrepancies between various samples (Table 3), in this study, only the possible sources for those VOCs are discussed exploratory. .

Nowadays, the mainstream technology currently used for the preparation of commercial RO membranes is interfacial polymerization on support materials via two steps (Gholami et al., 2018; Rana et al., 2015). In the first step, support membrane (the most common is Polysulfone (PSF), Fig. S1) is prepared according to the phase inversion method by casting their monomer solution on non-woven fabric. In the second stage, polyamide barrier layer on the top of support

membrane is prepared by in situ interfacial polymerization process between m-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase (Kong et al., 2011; Lalia et al., 2013; Mohan and Kullová, 2012).

VOC contamination could be introduced during the above steps. Usually, DMF was the most common solvent for dissolving PSF. However, in practice, the organic reagents used (e.g. TCM, Tol, DCA and etc.) might contain two or more solvents/additives to obtain a designed membrane for a particular application (Guillen et al., 2011; Herrero et al., 2014; Seung-Pyo et al., 2014). Thus, they should be the main sources of the high level residual VOCs (e.g. DMF) into RO membranes. Besides, the boundary reaction between MPD and TMC could also result in organic contamination, because the organic phase, primarily is Hex, is used as the solvent for dissolving TMC and as the cleaning agent for rinsing the membrane surface after the interfacial polymerization reaction (Gholami et al., 2018; Klaysom et al., 2013). The synthesis of the PSF raw materials could also be another possible sources of VOCs entering RO membranes. The nucleophilic substitution reaction between diphenol and bis(4-chlorophenyl)sulfone is a classical reaction that is widely used for commercial PSF production (Sahre et al., 2006). However, this reaction lead to the formation of the by-product water, which has a serious effect adverse to this reaction, for this reason, azeotropes such as Tol and Xyl are often synchronously added (Ates et al., 2011; Gao et al., 2017; Ma et al., 2020). Additionally, in industry production, the organic solvents used were often not pure enough, thus impurities in solvent (e.g., Xyl, PhH in Tol) may also be an important source of the VOCs (Han et al., 2015; Joshi et al., 2016).

In general, the results implied that the productive process of support materials could be the major source of the VOCs residual in RO membranes. Although many methods were available for removing the organic solvent, our study showed there still presented a considerable amount of residues. Thus, the RO membrane users always need to beware of the harmful effect of VOCs from their purity devices with a RO element.

3.4 Drinking water quality and risk assessment

To evaluate the migration of VOCs into effluent water, each experimental RO membrane was washed by 10 L of deionized water and then the effluent water was collected for the analysis of aqueous VOCs. Maximum contamination level (MCL) of drinking water from U.S. Environmental Protection Agency (USEPA), Ministry of Health, Labor and Welfare of Japan (MHLW), and Ministry of Health of China (MHC) were used to evaluate the potential adverse effect of VOCs in effluent water filtrated by RO membrane (JMHL, 2015; MHC/SAC, 2006; USEPA, 2018). In this study, concentration over MCL suggested the VOC was deemed to have a specific adverse effect on effluent water. Maximum VOCs in 10 L of effluent in measured samples are shown in Table 4. The results showed that the concentrations of DMK, Hex and Styrene were not detected in all samples. PhH, PhCl, ethylbenzene, and Xyl were far from the MCL, which indicated that the safety hazard for these substances was low.

DMF was often not limited in the drinking water quality criteria, and it possessed very high concentration in the initial effluent (780–5234 µg/L in 0 L). However, fortunately, with the increase of the effluent volume, its concentration rapidly decreased owing to its high solubility in water (Fig. S2), indicating it was not a key contaminant that was difficult to be removed by pre-washing. However, the concentrations of DCM, TCM, DCA, and Tol in effluent water decreased slowly with pre-washing (Fig. S2) and their concentration did have the risk to surpass the MCL after 10 L pre-washing. As DCM, TCM, DCA and Tol are all considered as the toxic substances which not only give the drinking water a bad taste or smell but also increase the risk of illness such as cancer, kidney, and nervous system problems (Al-Baldawi, 2018; Hrudey, 2009; Shestakova and Sillanpaa, 2013; Tavakoli Dastjerdi et al., 2017), users need to continue increasing the pre-washing volume to ensure their drinking water's quality.

3.5 Recommended VOC limit value

As the VOCs in RO membrane did affect the effluent water quality, it is necessary for practitioners to evaluate the safety limit values of VOCs in RO membrane. Species sensitivity distributions (SSDs) are commonly used to derive the limit values of contaminants in a field based on their limit values in a linked field (e.g. obtaining unknown soil thresholds for heavy metal from the food quality standard) (Ding et al., 2016; Ding et al., 2018). Countries around the world have set the drinking water standards to ensure the drinking water quality, but considering there were only limited data in our study and the SSDs is accomplished with the establishment of complex models and requires great experimental results (Wheeler et al., 2002), therefore, in this study, we tentatively assessed the safety contamination limits (SCLs) of VOCs in RO membrane by investigating the relationship between the VOC contents in RO membranes and their concentrations in effluent water.

The VOCs in effluent water that were higher in concentration than the one of the MCLs from USEPA, MHLW, or MHC were discussed. Figure 4 presents the relationship of the concentration of VOCs in 10 L effluent water with their contents in RO membranes. Clearly, with the increasing DCM, TCM, DCA, and Tol contents in RO membranes, their concentrations in effluent also proportionately increased significantly ($r > 0.995$, Fig. S3), indicating the proposed method can be used for calculation statistically. The MCL of each contaminant in drinking water is presented in Fig. 4, and the SCL of a VOC can be obtain by calculating the intersection points between the line of VOC MCL in drinking water with the column of VOC content in RO membranes. By this method, the SCLs of DCM, TCM, DCA, and Tol calculated from USEPA, MHLW and MHC were 1.2×10^3 – 4.9×10^3 , 6.3×10^3 – 7.4×10^3 , 2.6×10^2 – 2.0×10^3 , and 3.8×10^5 µg/kg, respectively. So, when the VOCs in RO membranes exceeded these values, their concentrations in the effluent within 10 L were more possible not able to reach the MCLs.

4. Conclusion

A method based on HS-GC/MS was developed for the analysis of common VOCs in RO membrane. The existence of matrix effect had a reverse effect on the accuracy of quantification, but the matrix-matched calibration established by VOC-free RO membranes provided good linearity, low detection, reproducibility and accuracy. Twelve VOCs were detected in RO membranes with contents in the range of N.D.–961 186 µg/kg and after pre-washing of the RO membranes, most of them showed no high-risk to the effluent quality. However, DCM, TCM, DCA, and Tol were more abundant in RO membranes and likely made water undrinkable. The investigation provide a basis for comparison for the contamination level in RO membranes and indicated that more accurate guideline values are necessary to be established to guarantee RO membrane quality.

Declarations

Ethical Approval: Not applicable.

Consent to Participate: Not applicable.

Consent to Publish: Not applicable

Author contributions Mingtao HOU: Conceptualization, Methodology, Writing-original draft. Huixue REN: acquisition, Methodology, Writing-review&editing. Wenqing CHENG: Investigation, Formal analysis, Supervision. Lingjie LI: Formal analysis, Validation. Shuai ZHANG: Validation, Visualization. Yanxue CHEN: Investigation, Supervision. Chunfeng YU: Supervision, Validation. Fangjun LI: Validation, Visualization. Naichao CHI: Supervision, Visualization. Wenxiu WANG : Validation, Visualization. Zhe DENG: Supervision, Validation. All authors read and approved the final manuscript.

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Availability of data and materials: All data generated or analysed during this study are included in this published article.

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Tables

Table 1 Curve slopes, coefficients and recoveries of different matrix matched calibration

Matrix materials	Blank (empty bottle)					Nylon Membrane				
	Slope	Coefficient	Recovery (%)			Slope	Coefficient	Recovery (%)		
			100/5000/ 50000 ng	500/10000/ 200000 ng	2000/20000/ 500000 ng			100/5000/ 50000 ng	500/10000/ 200000 ng	2000/20000/ 500000 ng
Acetone	348	0.9981	104	112	106	312	0.9990	97.3	104	115
Dichloromethane	319	0.9983	54.9	66.7	49.2	184	0.9986	95.3	115.7	85.3
Hexane	562	0.9991	108	116	107	547	0.9995	115	104	99.6
Chloroform	372	0.9998	46.6	69.3	45.7	205	1.0000	84.3	126	82.7
1,2-dichloroethane	272	0.9986	71.9	85.1	62.4	213	0.9983	91.5	108	79.4
Benzene	1111	0.9998	49.6	71.5	50.6	666	0.9990	82.6	119	84.4
Toluene	784	1.0000	67.3	79.6	54.1	501	0.9999	105	125	84.8
N,N-Dimethylformamide	96.7	0.9998	101	31.4	38.6	27.5	0.9988	46.0	64.3	57.5
Chlorobenzene	620	0.9993	39.8	57.9	43.6	325	0.9997	76.0	110	83.2
Ethylbenzene	885	0.9997	46.8	59.9	45.6	525	0.9995	78.8	101	76.8
m,p-xylene	754	0.9996	38.7	57.7	42.2	840	0.9992	68.6	102	74.9
o-xylene	335	0.9994	36.9	48.6	37.6	391	0.9993	71.3	93.9	72.6
Stryene	659	0.9991	42.2	47.7	40.4	362	1.0000	76.7	86.7	73.5

Table 2
Retention time, calibration curves, limits of detection (LODs) and quantitation (LOQs) for various compounds

Compound	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	Calibration curve equation	LOD (µg/kg)	LOQ (µg/kg)
Acetone	2.579	43	58	$Y = 292x - 9129$	3.87	12.9
Dichloromethane	3.035	84	86, 49	$Y = 158x + 17908$	14.3	47.7
Hexane	3.565	57	41/86	$Y = 487x - 38119$	4.93	16.4
Chloroform	4.745	83	85	$Y = 167x + 34017$	11.7	39.1
1,2-dichloroethane	5.435	62	98	$Y = 161x + 19777$	11.7	38.9
Benzene	5.380	78	/	$Y = 569x + 48990$	3.44	11.5
Toluene	8.060	92	91	$Y = 416x + 168095$	4.20	14.0
N,N-Dimethylformamide	9.985	73	44/58	$Y = 16.4x - 187770$	748	2493
Chlorobenzene	10.775	112	77, 114	$Y = 271x + 19603$	8.84	29.5
Ethylbenzene	11.080	91	106	$Y = 397x + 38815$	6.41	21.4
m,p-xylene	11.480	106	91	$Y = 621x + 93595$	6.20	20.7
o-xylene	12.640	106	91	$Y = 279x + 25565$	10.2	34.0
Styrene	12.720	104	78	$Y = 265x + 25085$	10.8	36.0

Table 3
VOCs distribution in experimental samples (µg/kg)

Compounds Samples	Acetone	Dichloromethane	Hexane	Chloroform	1,2- dichloroethane	Benzene	Toluene	N,N- dimethylformamide	Chlorobenzene
RO1	1193	N.D.	N.D.	N.D.	850	303	50449	129033	56.3
RO2	779	660	342	15072	N.D.	118	199366	961186	901
RO3	475	19.7	61.5	1287	882	166	400982	186220	9003
RO4	1133	1078	319	369	55.8	34.0	11981	90419	N.D.
RO5	587	N.D.	4348	N.D.	N.D.	64.3	10931	135879	1218
RO6	N.D.	N.D.	247	95.6	40.3	41.2	75371	86556.	3467
RO7	430	8121	57.0	352	74.6	N.D.	10190	153519	1990
RO8	507	N.D.	N.D.	12498	2471	40.3	84968	465429	16017
RO9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	15291	135532	647
RO10	N.D.	N.D.	1022	N.D.	N.D.	N.D.	41345	155801	N.D.
Mean	512	991	640	2969	439	77.1	90087	249957	3331
Proportion in mean ΣVOCs,%	0.14	0.27	0.17	0.80	0.12	0.02	24.2	67.3	0.90

Table 4
MCL values for VOCs in drinking water and the ratios of over MCL numbers in total sample numbers

Compound	Maximum value in 10L effluent µg/L	MCL µg/L			Over MCL numbers/total numbers		
		US's EPA	Japan's MHLW	China's MHC	US's EPA	Japan's MHLW	China's MHC
Acetone	N.D.	-	-	-	-	-	-
Dichloromethane	32.9	5	20	20	2/10	1/10	1/10
Hexane	N.D.	-	-	-	-	-	-
Chloroform	143	70	60	60	2/10	2/10	2/10
1,2-dichloroethane	37.9	5	4	30	3/10	3/10	1/10
Benzene	0.9	5	10	10	0/10	0/10	0/10
Toluene	420	1000	400	700	0/10	1/10	0/10
N,N- Dimethylformamide	28.0	-	-	-	-	-	-
Chlorobenzene	10.2	100	-	300	0/10	-	0/10
Ethylbenzene	0.2	700	-	300	0/10	-	0/10
Xylene	6.7	10000	400	500	0/10	0/10	0/10
Styrene	N.D.	100	-	20	0/10	-	0/10

Figures

Figure 1

Device of filtration test

Figure 2

Total Ion Chromatography (TIC) of the preliminary screening of VOCs in RO membrane

Figure 3

Effect of a) matrix modifier, b) incubation temperature and c) incubation time on the response of VOCs on mass spectrum detector, initial condition: incubation time = 80 °C, incubation time = 30 min, sample mass = 0.2 g.

Figure 4

VOCs concentration in 10 L effluent as a function of their content in RO membrane, a) DCM, b) TCM, c) DCA, d) Tol; Experimental condition: total flow rate = 0.5 L/min, ratio of purified water and waste water = 0.9 – 1.2.

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