

# Solid-phase extraction of sulfonylurea herbicides from water samples with single-walled carbon nanotubes disk

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**Abstract** This study presents a new, easily made and practical solid-phase extraction disk, a single-walled carbon nanotubes (SWCNTs) disk. The properties of the disk were evaluated by extracting large volumes of aqueous solution (500–3,000 mL) spiked with trace levels of sulfonylurea herbicides, metsulfuron-methyl, chlorsulfuron, bensulfuron-methyl, pyrazosulfuron-ethyl, and chlorimuron-ethyl. The adsorption of analytes on the SWCNTs disk was more favorable at pH 3.0, and the adsorbed sulfonylurea herbicides could be eluted completely with acetonitrile (1% acetic acid) solvent. The disks were stacked to enhance their extraction ability to analytes. The triple layered SWCNTs disks system showed excellent extraction efficiency when the sample volume was up to 3,000 mL. A comparative study was conducted with a commercial C<sub>18</sub> disk and an activated carbon disk. The SWCNTs disks showed an adsorption capacity comparable to sulfonylurea herbicides to the C<sub>18</sub> disk and activated carbon disk, but the analytes retained on the activated carbon disk were hardly desorbed. Finally, the triple layered SWCNTs disks system was used to pretreat 1,000 mL of several environmental water samples spiked with the analytes, and satisfactory recoveries (79–102%) were obtained. Detection limits of 1.1–7.2 ng L<sup>-1</sup> for analytes were achieved under the optimized conditions.

**Keywords** Solid-phase extraction · Single-walled carbon nanotubes disk · Sulfonylurea herbicides · Water sample

Sulfonylureas, introduced in 1982 by the Dupont Corporation, were developed for weed control in cereal crops all around the world [1, 2]. Because of their low application rates (10–40 g ha<sup>-1</sup>), and unprecedented herbicidal activity, they have become very popular as replacements for old high-application-rate herbicides [1–6]. However, the polar nature and fairly high water solubility of the sulfonylurea herbicides result in their high mobility; consequently they are detected in natural waters [4, 7]. Due to their high phytotoxicity and adverse impacts to mammals, they are regarded as potential water pollutants and presenting environmental risks, especially for crops [8, 9], aquatic plants and microorganisms [10, 11], and indirectly affect the whole trophic food web of aqueous biota, such as ponds.

The sulfonylurea residues in water samples have been extensively analyzed by LC methods using an ultraviolet (UV) detector or a diode array detector (DAD) [12–15]. Due to the fact that the UV detection often lacks the required sensitivity, a preconcentration step is required before HPLC–UV/DAD detection. Solid-phase extraction (SPE), widely accepted in environmental analysis [16], is usually selected for sample preparation to achieve adequate sensitivity for the analysis of herbicides in natural waters by HPLC [12, 17]. SPE is available in two formats generally, cartridges and disks. Incorporating adsorbents of small particle size, the disk format possesses a larger surface area than the cartridge, resulting in good mass transfer and fast flow rates [18]. In addition, the extraction efficiency of the disk was found to be sufficient for preconcentration of herbicides in natural waters [12]. A variety of adsorbents in disk format are available for the extraction of pesticides from water samples, and C<sub>18</sub> is one of the most widely used

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adsorbents [18, 19]. As a new kind of potent adsorbent, carbon nanotubes (including single-walled carbon nanotubes, SWCNTs, and multi-walled carbon nanotubes, MWCNTs) have been packed into cartridges to extract trace levels of organic compounds from environmental water samples. They have shown excellent extraction ability to various compounds with different polarity such as non-polar, moderate polar and highly polar compounds [20–26]. Here we report a novel approach in which SWCNTs adsorbents are assembled into a unique disk by means of a filtration process and firmly fixed on a piece of qualitative filter. The SWCNTs filter should be used as an effective SPE disk to preconcentrate trace sulfonylurea herbicides from water samples.

The objectives of this study were to demonstrate the validity of the SWCNTs disk for pretreating water samples, and then compare the extraction efficiency of the new disk with a commercial  $C_{18}$  disk and an activated carbon disk for sulfonylurea herbicide. Finally, the SWCNTs disks were used to analyze the presence of these compounds in several real water samples.

## Experimental

### Chemical and materials

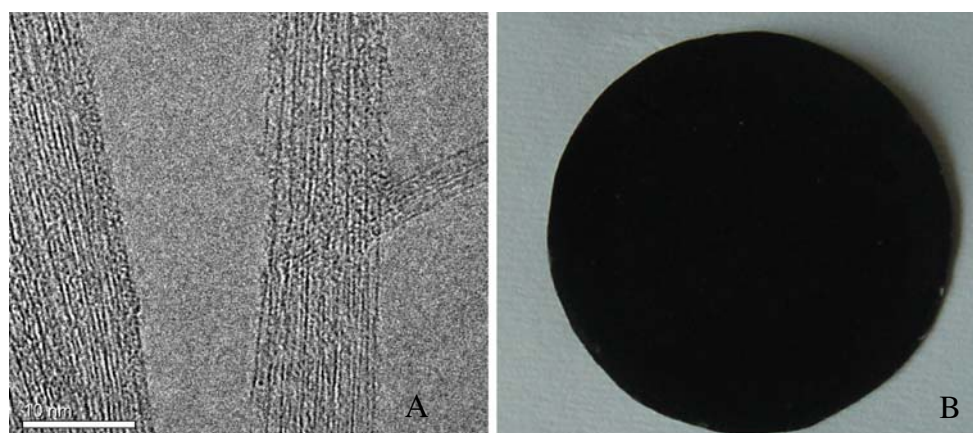
Metsulfuron-methyl, chlorsulfuron, bensulfuron-methyl, pyrazosulfuron-ethyl, and chlorimuron-ethyl at a concentration of  $100 \mu\text{g mL}^{-1}$  were purchased from the Institute of Environmental Protection and Monitoring, Department of Agriculture (Beijing, China, <http://www.aepi.org.cn>). Working solutions were prepared daily by appropriate dilution of the stock solutions with water. Ultrapure water was prepared in the lab using a Milli-Q Advantage A10 reagent water system from Millipore (Milford, MA, USA, <http://www.millipore.com>). HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany, <http://www.merck.com>). Sodium hydroxide and hydrochloric acid were of analytical grade, and supplied by Beijing Chemicals

Corporation (Beijing, China, <http://www.crc-bj.com>). SWCNTs were kindly donated by Nankai University, (Tianjin, China) and the SWCNTs were observed by transmission electron microscope (TEM; JEM-2011) under an acceleration voltage of 200 kV. The average external diameters and internal diameters were in the range of 1.5–2.5 and 1.0–2 nm, respectively (Fig. 1a). The specific surface area of SWCNTs was determined by the BET method, and it was shown to be  $297.72 \text{ m}^2 \text{ g}^{-1}$ . The qualitative filter paper (Hangzhou special paper industry Co. Ltd., HangZhou, China, <http://www.special-paper.com>) used to support SWCNTs adsorbent was 0.20–0.22 mm in thickness, and the diameter of the filter was 47 mm. The ENVI<sup>TM</sup>-18 DSK SPE disk and Empore<sup>TM</sup> activated carbon disk ( $\Phi=47 \text{ mm}$ , 500 mg, <http://www.sigmaaldrich.com>) were purchased from Supelco (Bellefonte, PA, USA) and 3 M Inc. (St. Paul, MN, USA, <http://www.3m.com>), respectively.

### Chromatographic conditions

The detection of sulfonylurea was performed by a Dionex SUMMIT<sup>®</sup> HPLC system (Dionex, USA, <http://www.dionex.com>) with a PDA-100 photodiode array detector. The separations were conducted on a Diamonsil<sup>®</sup>  $C_{18}$  column ( $250 \times 4.6 \text{ mm}$ ; particle size,  $5 \mu\text{m}$ ) (Dikma Technologies, Beijing, China, <http://dikma.gdbnet.cn>). Spectrophotometric detection of analytes was performed at 236 nm. Gradient separations for analytes were carried out using acetonitrile containing 0.5% acetic acid and acetonitrile–water (10:90, *V/V*) containing 0.5% acetic acid as the A and B solvents, respectively. The linear gradient profile was 10% A/90% B solvent maintained in the first 1.5 min and 37% A/63% B solvent in the next 2.5 min (held for 9 min), after which the mobile phase was returned to the initial conditions in 2 min. The flow rate was  $1 \text{ mL min}^{-1}$ . A personal computer equipped with a Chromeleon program for HPLC systems was used to acquire and process chromatographic data. The peak area was used as the analytical measurement.

**Fig. 1** SEM image (a) of SWCNTs and image SWCNTs disk (b)



### Preparation of SPE disk

To produce an SPE disk, 30 mg of SWCNTs adsorbent were ultrasonicated in 50 mL solution containing 5% of sodium dodecyl sulfate (SDS) for 30 min. After thorough dispersion of the SWCNT aggregates, the suspension was filtered through a 47-mm-diameter qualitative filter paper with a vacuum pump, thus the SWCNT adsorbents were distributed on the filter uniformly. The disk was washed with methanol and water successively to get rid of the residual SDS. The disk was allowed to dry at room temperature. The image of SWCNTs disk is shown in Fig. 1b.

### Solid-phase extraction procedure

The purified water or water samples were extracted onto the SWCNTs disks,  $C_{18}$  disk or activated carbon disk using a vacuum filtration apparatus. The glass filtration apparatus was washed with methanol and water before extraction. Prior to use, the disks were conditioned with 10 mL of methanol and then 10 mL of water. Then different volumes of samples spiked with five analytes were passed through the preconditioned disks. After sample extraction, the disks were allowed to air dry under vacuum for 5 min, then the analytes were eluted into test tubes using eluent. In this step, the eluent was rinsed down the sides of the glass filtration apparatus. One should be careful not to expose the surface of the  $C_{18}$  disk to air until the entire sample has been drawn through the disk during the disk conditioning and sample addition steps. The eluent was dried with a stream of nitrogen and reconstituted in 1.0 mL of acetonitrile. Aliquots (50  $\mu$ L) were injected into the HPLC system for analysis.

### Sampling

A tap water sample was collected from our laboratory, and a well water sample was from the campus of China Agricultural University. River water samples were collected from Jing Mi canal and Xiaoqinghe river (Beijing). The water samples were filtered immediately through 0.22- $\mu$ m filters to remove suspended solids, and then stored in dark glass containers at a temperature of 4 °C. Extraction of real water samples was carried out under the optimized method described earlier.

## Results and discussion

### SWCNTs disks

It is reported that the strong van der Waals interactions among SWCNTs lead to the highly adhesive structure with

tube ends embedded in the bundles [27]. When determined by BET, the  $N_2$  molecules hardly enter into the inner surface of the bundles [28], so the detected surface area of raw SWCNTs is significantly smaller than the theoretical BET area of 2,630  $m^2 g^{-1}$  [28]. Furthermore, the adhesive structure of the raw SWCNTs will lead to the uneven distribution of particles on the filter surface [29]. Therefore, to prepare an SPE disk, the tube ends must be released from the contorted bundles (debundling process). Both the surfactant treatment and ultrasonic process [27] can help the debundling of the particles; consequently, the bundle size will be reduced resulting in the enhancement of the SWCNTs external area. Zheng et al. [30] has proved that a sheet made of 37 mg of SWCNTs (47 mm in diameter, and 60  $\mu$ m in thickness) possessed a high specific surface area of  $\sim 700 m^2 g^{-1}$ . During the filtration process, the dispersed SWCNTs are distributed homogeneously on the filter surface. The interactions among the nanotubes are so strong that the stress generated by nanotube sheets perpendicular to the disk surface is about five times that of a human skeletal muscle [31]. Therefore, the nanotubes can be fixed on the filter (even possessing large pore size) surface without leaking or peeling during the process of filtration or sample loading. In our study, the sheet was typically 30  $\mu$ m in thickness, as measured with a micrometer, and had density of  $\sim 0.5 g cm^{-3}$  on the basis of the mass, area, and thickness of the sheet.

### Effect of solution pH

The selected analytes were weak acids in nature with the  $pK_a$  value varying from 3.6 to 5.2. As shown in Table 1, the solubility of sulfonyleurea herbicides in water were increased drastically with the solution pH, and when the pH was up to 7.0, the solubility of metsulfuron-methyl, chlorsulfuron and chlorimuron ethyl was much higher than 1,000  $mg L^{-1}$ , indicating the high polarity of the analytes. Since the retention of sulfonyleurea herbicides on the SWCNTs adsorbents was mainly based on hydrophobic interaction, adsorption of the analytes is preferable in their uncharged state. Therefore, the sample pH would play an important role in the enrichment of the sulfonyleurea herbicides. A series of experiments were designed to investigate the influence of sample pH over the range of pH 2.5–8.5. According to the results shown in Fig. 2, the adsorption of all the analytes was more favorable in acidic solution. For metsulfuron-methyl, total recovery was achieved at pH 2.5, which decreased to 95% at pH 3.0, after which the recovery dropped clearly with the increase of pH; while the abrupt decrease of the recoveries for other analytes occurred when the pH of solution was higher than 4.6. At pH 8.2, hardly any of the analytes was retained by the disks. So pH 3.0 was selected in the following experiment.

**Table 1** Solubility, dissociation constants ( $pK_a$ ) and octanol/water partition constants ( $\log K_{ow}$ ) of the analytes

|                      | Solubility in water ( $\text{mg L}^{-1}$ ) [12, 32] <sup>a,b,c</sup> | $pK_a$ [12, 32] <sup>a,b,c</sup> | $\log K_{ow}$ (pH 7) [12] <sup>a,c</sup> |
|----------------------|--|----------------------------------|--|
| Metsulfuron-methyl   | 270 (pH 5); 9,500 (pH 7)   | 3.7                              | -1.74                                    |
| Chlorsulfuron        | 7,000  | 3.6                              | -1.34                                    |
| Bensulfuron-methyl   | 120  | 5.2                              | 0.62                                     |
| Pyrazosulfuron-ethyl | 14   | 3.7                              | 1.3                                      |
| Chlorimuron ethyl    | 1.5 (pH 2.5); 4.1 (pH 4.2); 9.0 (pH 5.0); 1,200 (pH 7.0)             | 4.2                              | 0.11                                     |

<sup>a</sup> <http://www.herts.ac.uk/aeru/footprint/en.htm>

<sup>b</sup> <http://www.essenagrochem.com/products.htm>

<sup>c</sup> <http://pmep.cce.cornell.edu/profiles/herb-growthreg/cacodylic-cymoxanil.htm>

### Effect of sample volume

Since the breakthrough volume is an important factor for SPE to obtain reliable and reproducible analytical results, different volumes (500–3,000 mL) of purified water spiked with  $0.5 \text{ ng mL}^{-1}$  of each analyte were preconcentrated by different layered disk systems. The results showed that the single-layered disk system had low retention ability for most of the analytes when large volumes of sample were loaded (see Fig. 3a). The extraction ability of the disks was enhanced greatly when a double-layered disk system was used. The recoveries of all analytes remained constant until the sample volume was larger than 1,500 mL, after which the recoveries decreased as the sample volume increased (Fig. 3b). For the triple-layered disk system, a striking retention capability for sulfonylurea herbicides was observed, and the recoveries of all the analytes were higher than 90% when the sample volume was up to 3,000 mL (Fig. 3c). In general, the extraction ability went up obviously with the

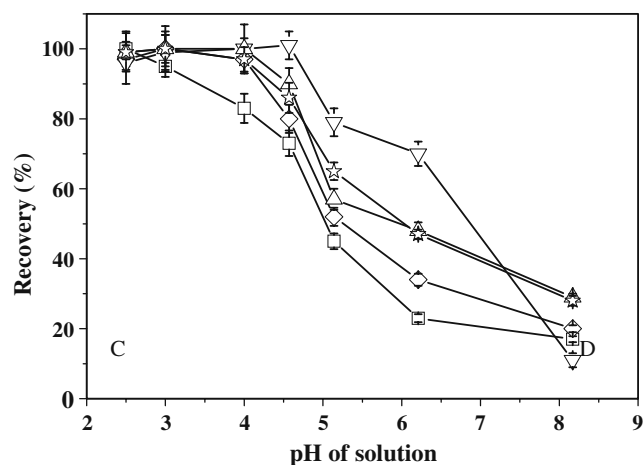
increase in the number of disks. However, for bensulfuron-methyl and chlorimuron-ethyl, the double-layered disk system showed the same high enrichment efficiency as the triple-layered disks system.

### Effect of flow rate

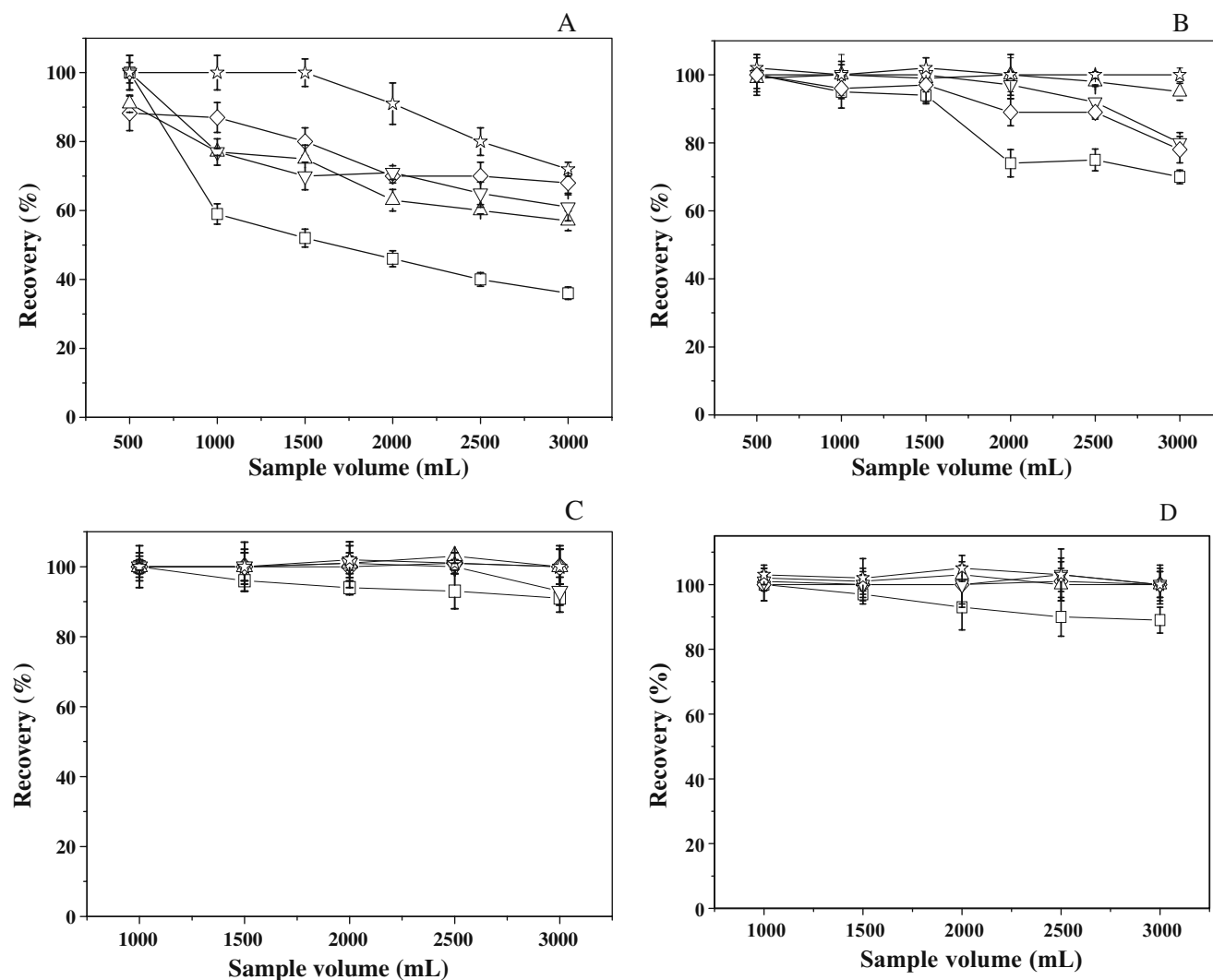
Flow rate was another important factor that influenced the enrichment efficiency and controlled the extraction time. The sample flow rate could be adjusted by the manifold vacuum pressure. For the single-layered disk system, the maximum flow rate of  $150 \text{ mL min}^{-1}$  could be achieved without decreasing the retention of the analytes. As to the double-layered or triple-layered disk system, the maximum flow rate decreased to approximately  $50 \text{ mL min}^{-1}$ , and the recoveries of all the analytes remained constant as the sample loading rate was varied in the range of 10–50  $\text{mL min}^{-1}$ . Actually, the maximal flow rate of the triple-layered disk system was comparable to the flow rates of  $C_{18}$  and activated carbon disks achieved with our vacuum pump.

### Comparison study

The extraction ability of SWCNTs disks to sulfonylurea herbicides was compared with a commercial  $C_{18}$  disk and activated carbon disk ( $\Phi=47 \text{ mm}$ , 500 mg). The adsorbed analytes on SWCNTs disks and a  $C_{18}$  disk could be completely desorbed with acetonitrile containing percent acetic acid. However, 90% of trapped herbicides could not be eluted from the activated carbon disk by acetonitrile, methanol, acetone, tetrahydrofuran or methylene chloride. After extraction by activated carbon disk, the percolate of different volumes was collected and preconcentrated with the  $C_{18}$  disk, respectively. None of the analytes was detected in the percolate, indicating that there was an irreversible interaction existing between sulfonylurea analytes and activated carbon adsorbents. Therefore, regardless of the high adsorption ability of activated carbon to sulfonylurea compounds, it could not be utilized to pretreat environmental water samples for the detection of sulfonylurea herbicide.



**Fig. 2** Effect of solution pH on the recoveries of target compounds extracted with triple-layered disk system. *Square*, metsulfuron-methyl; *diamond*, chlorsulfuron; *triangle*, bensulfuron-methyl; *inverted triangle*, pyrazosulfuron-ethyl; *star*, chlorimuron-ethyl. Solution volume, 1,000 mL; concentration of each analyte,  $0.5 \text{ ng mL}^{-1}$



**Fig. 3** Effect of sample volumes on the recoveries of analytes preconcentrated by different layered SWCNTs disk systems and an ENVI™-18 DSK  $C_{18}$  disk. **a** Single-layered disks; **b** double-layered disks; **c** triple-layered disks; **d**  $C_{18}$  disk. *Square*, metsulfuron-methyl;

*diamond*, chlorsulfuron; *triangle*, bensulfuron-methyl; *inverted triangle*, pyrazosulfuron-ethyl; *star*, chlorimuron-ethyl. Concentration of each analyte,  $0.5 \text{ ng mL}^{-1}$

The comparison of SWCNTs disks and  $C_{18}$  disk is shown in Fig. 3. Similar to the triple-layered disk system, the  $C_{18}$  disk displayed excellent retention ability to most of the analytes when the sample volume was up to 3,000 mL. For bensulfuron-methyl and chlorimuron-ethyl, the extraction ability of double-layered disks was even comparable with

the  $C_{18}$  disk. It should be mentioned that the amount of SWCNTs adsorbent in each disk was only 30 mg, which was far less than the amount of  $C_{18}$  adsorbent (500 mg) in one disk. Compared with the work by Zhou et al. [13], the extraction ability of the triple-layered disk system was comparable or superior to the MWCNTs cartridge (100 mg

**Table 2** Analytical parameters of the HPLC–DAD method after SPE with triple-layered SWCNTs disk system

|                      | Linear range ( $\text{ng L}^{-1}$ ) | Calibration equations | $R^2$  | Detection limit ( $\text{ng L}^{-1}$ ), ( $S/N=3$ ) |
|----------------------|-------------------------------------|-----------------------|--------|---|
| Metsulfuron-methyl   | 30–3,000                            | $y=0.0015x+0.0228$    | 0.9975 | 6.2   |
| Chlorsulfuron        | 30–3,000                            | $y=0.0017x+0.0134$    | 0.9995 | 1.1   |
| Bensulfuron-methyl   | 30–3,000                            | $y=0.0013x+0.0627$    | 0.9969 | 6.5   |
| Pyrazosulfuron-ethyl | 30–3,000                            | $y=0.0015x-0.0224$    | 0.9998 | 2.8   |
| Chlorimuron-ethyl    | 30–3,000                            | $y=0.001x+0.0096$     | 0.9979 | 7.2   |

**Table 3** Recoveries (percent)  $\pm$  standard deviation (based on three replicates) of real water samples spiked with 200 ng L<sup>-1</sup> of each target analyte

|                      | Well water  | Tap water   | Jing Mi canal | Xiaoqinghe River |
|----------------------|-------------|-------------|---------------|------------------|
| Metsulfuron-methyl   | 99 $\pm$ 2  | 102 $\pm$ 2 | 93 $\pm$ 1    | 79 $\pm$ 1       |
| Chlorsulfuron        | 99 $\pm$ 2  | 99 $\pm$ 1  | 97 $\pm$ 3    | 84 $\pm$ 3       |
| Bensulfuron-methyl   | 102 $\pm$ 2 | 96 $\pm$ 5  | 95 $\pm$ 4    | 76 $\pm$ 3       |
| Pyrazosulfuron-ethyl | 99 $\pm$ 3  | 101 $\pm$ 3 | 101 $\pm$ 1   | 85 $\pm$ 4       |
| Chlorimuron-ethyl    | 95 $\pm$ 2  | 101 $\pm$ 1 | 99 $\pm$ 3    | 91 $\pm$ 4       |

Triple-layered disk system

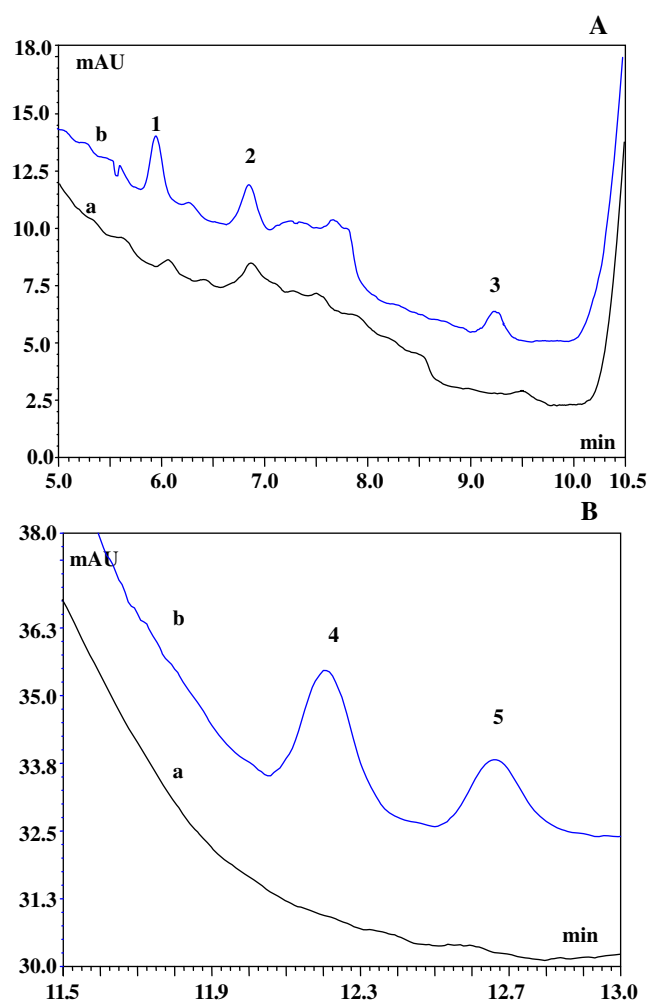
adsorbent). So the satisfactory recoveries of the polar analytes on layered disks demonstrated the outstanding extraction capability of SWCNTs disks.

#### Analytical performance and sample analyses

In this experiment, a triple-layered disk system was used to preconcentrate 1,000 mL of water samples. Samples were acidified to pH 3 with dilute hydrochloric acid. Under the optimal conditions, some important parameters of the proposed method, such as linear range, correlation coefficient and detection limits, were investigated. The results are listed in Table 2. It could be seen that there was an excellent linear correlation between the peak area and concentration from 30 to 3,000 ng L<sup>-1</sup> for all the analytes. The detection limits of the sulfonylurea herbicides were obtained based on the signal as three-fold the baseline noise ( $S/N=3$ ) for extraction of 1,000 mL water samples. The results showed that the detection limits for all the analytes were less than 10 ng L<sup>-1</sup>. The LOD for chlortoluron was lower than that obtained by extracting from 1,000 mL of purified water sample with C<sub>18</sub> Empore disk (determined by DAD-HPLC) [15] or by SPE with an Oasis HLB cartridge from 500 mL pure water samples [4]. Strikingly low LODs of sulfonylurea herbicides were also reported by Zhu et al. [5] (less than 10 ng L<sup>-1</sup>, SPE by a molecularly imprinted polymer cartridge from 1,000 mL of tap water) and Corcia et al. [14] (less than 2 ng L<sup>-1</sup>, achieved with a graphitized carbon blacks cartridge pretreating from 4,000 mL of drinking water samples), the LODs of sulfonylurea herbicides in our study were equivalent to these reports.

The proposed method had been applied to the analysis of several environmental water samples. None of the analytes were detected in these samples. To evaluate the accuracy of the proposed method, 1,000 mL of environmental water samples spiked with the mixture of analytes at 200 ng L<sup>-1</sup> were preconcentrated. Table 3 shows the mean recoveries and standard deviations of herbicides spiked to different water samples. The recoveries obtained from well water, tap water and Jing Mi canal samples were almost 100%. However, a matrix effect was observed on the extraction of sulfonylurea from Xiaoqinghe river water sample. It has been reported that the low pH of the water sample may

increase the retention of humic and fulvic acids [11], therefore the extraction efficiency of SWCNTs disks was influenced when samples with more complex matrices were pretreated. The chromatograms of the Xiaoqinghe river sample and its spiked solution are shown in Fig. 4.



**Fig. 4** a–b LC–DAD chromatograms of Xiaoqinghe river samples preconcentrated by triple-layered SWCNTs disks. (a) Xiaoqinghe river sample, (b) Xiaoqinghe river sample spiked with 0.20 ng mL<sup>-1</sup> of each compound. 1, metsulfuron-methyl; 2, chlorsulfuron; 3, bensulfuron-methyl; 4, pyrazosulfuron-ethyl; 5, chlorimuron-ethyl. Volume of water samples, 1,000 mL; volume of eluent, acetonitrile containing 1% acetic acid, 10 mL

## Conclusion

A new kind of solid-phase extraction disk (SWCNTs disk) has been invented in our laboratory. The process of preparing a disk is rather simple. A comparison study showed that the SWCNTs disks exhibited similar extraction ability for sulfonylurea herbicides as an activated carbon disk and C<sub>18</sub> disk; but unlike the activated carbon disk, the analytes adsorbed on SWCNTs disks could be desorbed easily with acetonitrile (1% acetic acid). Due to the reasonable thickness, the disks could be stacked to treat samples together without leaking. It could be concluded that excellent recoveries would be achieved for different analytes by using different layered SWCNTs disk systems according to the hydrophobicity of the analytes. In summary, the proposed new solid-phase extraction disk showed great analytical potential for SPE of large volumes of real water samples.

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