Simultaneous determination of 11 antiseptic ingredients in surface water based on polypyrrole decorated magnetic nanoparticles†

Mengyan Zhang,a Kaoqi Lian, a Lianfeng Ai,b Weijun Kang b,*a and Tangjuan Zhao*a

With the emergence and spread of coronavirus COVID-19, the use of personal cleansing, medical and household disinfectant products have increased significantly. In this work, a new magnetic solid-phase extraction (MSPE) method for the determination of 11 antiseptic ingredients in surface water by high performance liquid chromatography-mass spectrometry (HPLC-MS/MS) for 6 months based on Fe3O4@Ppy magnetic nanoparticles (MNPs) was established. The MSPE method possessed the advantages of simple processing, little time consumption and less organic solvent consumption, and the MNPs could be reused several times. The analytical parameters influencing the extraction efficiency, such as sample pH, amount of MNPs and extraction time, were optimized in detail. It was indicated that the method had satisfactory linealities in the range of 0.50 to 1000.0 μg L⁻¹ with the correlation coefficients (r) higher than 0.9996. Additionally, satisfactory spiked recoveries were achieved in the range of 80.21–107.33% with relative standard deviations (RSDs) from 1.98% to 8.05%. The limits of detection (LODs) and limits of quantitation (LOQs) were in the range of 0.20 to 2.0 μg L⁻¹ and 0.50 to 5.0 μg L⁻¹. Therefore, the developed MSPE-HPLC-MS/MS method has high selectivity and stability, and satisfactory quantitative capability for the antiseptic ingredients in surface water. Furthermore, this method can provide relevant technical support for the development of surface water standards.

1. Introduction

National medical institutions and other public places demand large-scale and high-frequency disinfection in the COVID-19 epidemic outbreak in our country. The amount of household disinfectants and personal cleaning products used also presents a significant increase trend. The above factors contribute to an increased content of antiseptic ingredients in the environment. In 2020, iiMedia Research showed that disinfection frequency was 1–3 times per day for 43% of Chinese residents and 1–5 times a week for 51% of Chinese residents during the new outbreak period. According to the reports of the Europe Disinfectant Sprays and Wipes Market 2019–2028 and the Middle East and Africa Disinfectant Sprays and Wipes Market 2019–2028, the use of disinfectant sprays and wipes shows an upward trend, in places such as Italy, the United Kingdom and Saudi Arabia. Several antiseptic ingredients in these disinfection products have been identified as environmental endocrine disrupting chemicals (EDCs).1,2 Therefore, the content of antiseptic ingredients in environmental water deserves our attention. At present, the main component of disinfectant products usually used for medical, environmental disinfection and personal care is halide.3–7 Among the halide, halogen-containing quaternary ammonium salt, as a kind of cationic surfactant, was first synthesized by the Jacob's group in 1915.8 Quaternary ammonium compounds (QACs) play a positive role in disinfection, but they also bring some negative effects to the ecological environment, for they can be strongly adsorbed on negatively charged surfaces, sludge, soil, sediments, and biological cell membranes.9,10 Benzalkonium chloride (BAC), as one of the most representative disinfectants in QACs, can cause DNA damage to animals and plants, produce antagonism with anticancer drugs, and cause reproductive toxicity and genotoxicity.11,12 Triclosan (TCS) and triclocarban (TCC) are widely used in personal care products as excellent antimicrobial and disinfectant. Research showed that TCS and TCC were not only frequently detected in various environmental media,13–15 but also could be enriched in the organism and induced a variety of toxic effects.16,17 According to the reasons, it is urgent to establish high-efficiency methods for the pretreatment and determination of disinfectants in environmental water during the outbreak of COVID-19 to monitor the healthy and sustainable development of the ecosystem.

At present, QuEChERS,18,19 solid phase extraction (SPE),20,21 dispersive liquid–liquid microextraction (DLLME),22,23 and liquid
phase microextraction (LPME)\textsuperscript{24,25} are commonly used for purification and enrichment of disinfectants in different matrices. Although these pretreatment methods have high recovery, the required sample volumes are generally large, and the operation is time-consuming. The magnetic solid phase extraction (MSPE), as a novel pattern of SPE, was often employed to enrich and purify of analytes in complex matrices due to its feather of simplicity, efficiency, rapidity, and environment-friendly.\textsuperscript{26,27} As a type of conducting polymer (CP), polypyrrole (PPy) possesses advantages of low toxicity, low cost, and ease of preparation.\textsuperscript{28,29} PPy has been used to extract benzenoid organic compounds by strong π–π, hydrogen bonding interactions, and hydrophobic.\textsuperscript{30,31} In SPE, PPy adsorbent usually needs to be separated from matrices by centrifugation or filtration, which reduce recovery. In this study, PPy was introduced on the surface of Fe\textsubscript{3}O\textsubscript{4} to prepare Fe\textsubscript{3}O\textsubscript{4}@PPy which can be easily separated from matrices by applying an external magnetic field.

Antiseptic ingredients are often analyzed by liquid chromatography (LC),\textsuperscript{32} capillary electrophoresis (CE),\textsuperscript{33} gas chromatography-mass spectrometer (GC-MS),\textsuperscript{34} gas chromatography triple quadrupole tandem mass spectrometer (GC-MS/MS),\textsuperscript{35} and liquid chromatography-time-of-flight-mass spectrometry (LC-TOF-MS).\textsuperscript{36} Compared with GC and LC, high performance liquid chromatography triple quadrupole tandem mass spectrometer (HPLC-MS/MS) has advantages of shorter time, facile operation, and higher sensitivity.\textsuperscript{37,38} In addition, its measurement is more accurate, and the detection limit is lower than that of LC-TOF-MS.

In this work, the Fe\textsubscript{3}O\textsubscript{4}@PPy was prepared successfully and applied for the extraction of 11 antiseptic ingredients in surface water matrices. The main parameters affecting the extraction efficiency were optimized in detail. Then the MSPE-HPLC-MS/MS method was established and utilized to the determination of antiseptic ingredients from surface water samples for environmental monitoring.

2. Experimental

2.1. Chemicals and reagents

Triclocarban (TCC), bromochlorophen (BCP), hexachlorophene (HCP), and 4-chloro-3-methylphenol (PCMP) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Triclosan (TCS), benzethonium chloride (BEC), dodecyl dimethyl benzylammonium chloride (C12-BAC), tetradecyl dimethyl benzylammonium chloride (C14-BAC) and cetyl dimethyl benzylammonium chloride (C16-BAC) were purchased from BePure (Manhattan Biotechnology Co., Ltd. Beijing, China). Clofucarban (CFC) was purchased from J&K Chemical (Beijing, China), benzalkonium chloride (BAB) was brought from National Institutes for Food and Drug Control (Beijing, China). The purity of the above standard products are more than 98.0%.

Methanol and acetonitrile (Merck, Darmstadt, Germany) are all HPLC grade. Formic acid and hydrochloric acid were purchased from Dikma Technologies (Lake Forest, CA, USA). Ammonium acetate, pyrrole (Py), sodium p-toluenesulfonate (NaPTS), iron(m) chloride hexahydrate (FeCl\textsubscript{3}·6H\textsubscript{2}O), iron(n) chloride tetrahydrate (FeCl\textsubscript{3}·4H\textsubscript{2}O), ammonium hydroxide solution (25–28 wt%) and polyvinyl alcohol (PVA) were purchased from J&K Chemical (Beijing, China). Ultrapure water (Millipore, Bedford, MA) was used throughout the work.

2.2. Preparation of standard and working solutions

Standard stock solutions of each individual drug (TCC, TCS, CFC, BCP, HCP, PCMP, C12-BAC, C14-BAC, C16-BAC, BAB and BEC) were prepared in methanol at a concentration of 10 g L\textsuperscript{-1} and stored in a refrigerator at 0–4°C prior to analysis. The matrix calibration standard working solution was prepared from the above solution by dilution with blank sample extract.

2.3. Synthesis of Fe\textsubscript{3}O\textsubscript{4}@PPy

Fe\textsubscript{3}O\textsubscript{4} was synthesized by our previous studies and the dosage of reagents was optimized in this work.\textsuperscript{39} 10.42 g of FeCl\textsubscript{3}·6H\textsubscript{2}O and 8.44 g of FeCl\textsubscript{2}·4H\textsubscript{2}O were dissolved in 500 mL of ultrapure water. After complete dissolution, it was filtered through 0.45 μm filter membrane. After added 1.70 mL hydrochloric acid, the solution was sonicated for 30 min under nitrogen. A certain amount of ammonia water was added to make the pH > 10.0 under nitrogen, and the mixed solution was stirred at 800 rpm min\textsuperscript{-1} for 40 min at 80°C in a water bath. The resultant nanoparticles were collected by external magnet, and then washed with absolute ethanol for several times and dried at 60°C for 12 h in a vacuum oven.

Subsequently, Fe\textsubscript{3}O\textsubscript{4}@PPy was synthesized by chemical oxidative polymerization method.\textsuperscript{39-41} 0.60 g of NaPTS and 0.65 g of Fe\textsubscript{3}O\textsubscript{4} were introduced into a three-necked flask and then 100 mL water was added to sonicate for 15 min to get homogeneous dispersion. Subsequently, 0.80 mL Py monomer was added and stirred for 30 min. Then, 40 mL PVA solution containing 0.80 g FeCl\textsubscript{3}·6H\textsubscript{2}O was dropped slowly into the reaction solution and stirred for 12 h at room temperature. The product was washed with absolute ethanol and water successively, and finally dried in a vacuum oven at 60°C for 8 h.

2.4. Sample collection and MSPE processes

A total of 18 water samples from Hutuo River in Shijiazhuang urban area (Hebei province, China.) were collected, each of which was at least 500 mL. Choose three sampling points to collect water samples continuously for 6 months (Table S1). All samples were preserved at 4°C.

The schematic of the MSPE processes are followed as: a total of 20.0 mL sample of water was added to a tube and centrifuged at 8000 rpm for 10 min at 4°C. Then 10.0 mL of supernatant was transferred to a 25 mL conical flask containing 10.0 mg Fe\textsubscript{3}O\textsubscript{4}@PPy. The pH of the water sample was adjusted to 8.0 by addition of 1.0 mol L\textsuperscript{-1} NaOH. After sonication for 10 s, the mixture was oscillated for 20 min for achieving the absorption equilibrium. Afterwards, the analytes-Fe\textsubscript{3}O\textsubscript{4}@PPy were separated from the mixture with an external magnet. The analytes retained on the MNPs were eluted with 1.0 mL methanol by vortex for 1.5 min. Next, the eluent was dried under a gentle N\textsubscript{2} flow at 40°C and redissolved in 100.0 μL of initial mobile phase.

2.5. Analysis of antiseptic ingredients

A total of 11 antiseptic ingredients were analyzed in water samples using an Agilent 1290 HPLC system equipped with a G1312B binary pump, a G1315A diode array detector, a G1316A autosampler, and a G1315C thermostat (Agilent, USA). The mobile phase of water and methanol (10:90, v/v) was used at a flow rate of 0.8 mL min\textsuperscript{-1}. The standard MSPE-HPLC method was established for 11 antiseptic ingredients as listed in Table S1. The analytes were separated on a Phenomenex Phenomenex C18 column (150 mm × 4.6 mm, 5 μm, USA) using a gradient elution.

The injection volume was 10 μL, and the column temperature was set at 35°C. The detection wavelength was 268 nm. The limits of detection (LOD) and limits of quantification (LOQ) were determined as three and ten times the signal-to-noise ratio (S/N), respectively. The recovery of the analytes was evaluated from three different concentration levels (5, 20, 100 mg L\textsuperscript{-1}) with each concentration spiked in triplicate to 18 water samples. The average recoveries were in the range of 78.4%–118.5% for 11 antiseptic ingredients. The correlation coefficients were in the range of 0.9997–0.9999. The RSDs of replicates with the same concentration level were in the range of 1.0%–11.5%

3. Results and discussion

3.1. Performance test of Fe\textsubscript{3}O\textsubscript{4}@PPy sorbent

The sorption efficiency of Fe\textsubscript{3}O\textsubscript{4}@PPy sorbent was tested with water samples spiked with 11 antiseptic ingredients at the concentration of 20 mg L\textsuperscript{-1}. The results in Table S2 show that the Fe\textsubscript{3}O\textsubscript{4}@PPy sorbent could effectively adsorb the analytes from the water samples.

3.2. Optimization of MSPE parameters

In this work, the operational parameters of MSPE method were optimized by central composite design (CCD) for the extraction of 11 antiseptic ingredients from surface water samples.

The optimal conditions of ultrasonic time, stirring time, stirring speed, sonication time, sample volume, adsorbent dosage, and pH were designed and optimized (Table S3). Under optimal conditions, the RSDs were less than 10%.

3.3. Analytical performance of MSPE-HPLC method

The precision (RSD) of the replicate analysis for the analytes were lower than 10% and the LODs were in the range of 0.27–0.57 μg L\textsuperscript{-1} (Table S4). The recoveries of the analytes were in the range of 75.5%–115.4%.

3.4. Application of MSPE-HPLC method

The method was applied to the analysis of antiseptic ingredients in surface water samples (Table S5). The quantities of the analytes were in the range of 0.98–26.0 μg L\textsuperscript{-1}.

4. Conclusion

A high-performance magnetic solid phase extraction method was established and utilized for the determination of antiseptic ingredients from surface water samples for environmental monitoring. The Fe\textsubscript{3}O\textsubscript{4}@PPy sorbent was synthesized successfully and applied for the extraction of 11 antiseptic ingredients in surface water matrices. The main parameters affecting the extraction efficiency were optimized in detail. Then the MSPE-HPLC-MS/MS method was established and utilized to the determination of antiseptic ingredients from surface water samples for environmental monitoring.
solution. Finally, the redissolved solution was filtered through a 0.22 μm filter membrane before HPLC-MS/MS analysis.

2.5. HPLC-MS/MS analysis

2.5.1. Instrument. Analysis of antiseptic ingredients were performed on a HPLC-MS/MS system consisting of an AB SCIEX Triple Quad™ 5500, and HPLC (AB SCIEX™, Foster City, CA) equipped with a ZORBAX Eclipse XDB-C18 column (4.6 mm × 50 mm, 1.8 μm. Agilent Technologies, Palo Alto, Calif.). Before injection, the column was perfused with an initial mobile phase until the pressure fluctuations remained steady. The morphology data of the Fe₃O₄ and Fe₃O₄@PPy was performed by an increase to 75% B for 6.5 min, then increased to 90% B within 0.1 min rapidly and maintained 90% B for 0.9 min, returned to the initial mobile phase ratio and maintained for 3.0 min for column repair. This entire process took 12.0 min at 0.3 mL min⁻¹ flow rate.

2.6. Method validation

The method was validated by evaluating the contents of linearity, limits of detection (LOD), limits of quantification (LOQ), accuracy, precision, and robustness. The calibration plots were generated by plotting the peak area of MS spectra versus concentration for each analyte. The sensitivity of the method was evaluated by LOD and LOQ. The accuracy of the method was expressed by the recovery, which was calculated by the following formula: recovery (%) = detected amount/added amount × 100%. The precision of the proposed method was evaluated by inter-day and intra-day relative standard deviations (RSDs). The robustness was tested using four certain conditions.

3. Results and discussion

3.1. Characterization for Fe₃O₄@PPy

The magnetic material was characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectrometer (FT-IR Spectrometer). Fe₃O₄ (Fig. 1a) and Fe₃O₄@PPy (Fig. 1b) were characterized by TEM.

Fig. 1 TEM images of (a) Fe₃O₄ and (b) Fe₃O₄@PPy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
<th>Precursor ion (m/z)</th>
<th>Product ion (m/z)</th>
<th>DP (V)</th>
<th>CE (eV)</th>
<th>ESI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCMP</td>
<td>3.39</td>
<td>140.9</td>
<td>35.1⁵, 105.0</td>
<td>−22.26, −35.97</td>
<td>−91.54, −105.14</td>
<td>−</td>
</tr>
<tr>
<td>C12-BAC</td>
<td>4.11</td>
<td>304.2</td>
<td>91.0⁵, 212.3</td>
<td>80.03, 81.87</td>
<td>38.07, 30.16</td>
<td>+</td>
</tr>
<tr>
<td>BAB</td>
<td>4.31</td>
<td>412.3</td>
<td>90.8⁶, 72.0</td>
<td>78.06, 79.01</td>
<td>83.79, 33.50</td>
<td>+</td>
</tr>
<tr>
<td>BEC</td>
<td>4.32</td>
<td>412.0</td>
<td>72.0⁶, 320.0</td>
<td>135.0, 124.91</td>
<td>34.80, 38.07</td>
<td>+</td>
</tr>
<tr>
<td>C14-BAC</td>
<td>6.50</td>
<td>332.0</td>
<td>91.0⁶, 240.5</td>
<td>110.68, 115.00</td>
<td>57.71, 30.39</td>
<td>+</td>
</tr>
<tr>
<td>TCC</td>
<td>7.11</td>
<td>313.0</td>
<td>160.0⁵, 126.0</td>
<td>−68.96, −56.77</td>
<td>−31.60, −24.84</td>
<td>−</td>
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<tr>
<td>TCS</td>
<td>7.45</td>
<td>286.7, 287.7</td>
<td>35.1⁶</td>
<td>−60.80, −88.96</td>
<td>−19.17, −33.36</td>
<td>−</td>
</tr>
<tr>
<td>CFC</td>
<td>7.52</td>
<td>347.2, 349.2</td>
<td>194.1⁶</td>
<td>−129.11, −135.12</td>
<td>−22.17, −15.04</td>
<td>−</td>
</tr>
<tr>
<td>BCP</td>
<td>9.21</td>
<td>424.9</td>
<td>204.9⁶, 78.9</td>
<td>−69.4, −59.33</td>
<td>−37.76, −165.68</td>
<td>−</td>
</tr>
<tr>
<td>C16-BAC</td>
<td>9.78</td>
<td>360.2</td>
<td>91.0⁶, 268.4</td>
<td>70.92, 80.38</td>
<td>60.88, 32.17</td>
<td>+</td>
</tr>
<tr>
<td>HCP</td>
<td>10.82</td>
<td>403.3</td>
<td>195.0⁵, 367.0</td>
<td>−78.12, −71.06</td>
<td>−31.36, −23.8</td>
<td>−</td>
</tr>
</tbody>
</table>

Table 1 Retention times and mass spectrometric parameters of 11 analytes

a Quantitative ion.
The black part in the middle is Fe₃O₄ MNPs. The light part of the outer layer is PPy, which was formed by the polymerization of Py monomers. The co-ion effect of Fe³⁺ oxidant is the main reason for Fe³⁺ aggregation on the surface of Fe₃O₄ MNPs, and it is also the reason for the complexation of Fe³⁺ with PPy. The result of the XRD patterns of Fe₃O₄ and Fe₃O₄@PPy was showed in Fig. S1. The typical peaks of the MNPs were observed at 2θ = 30.22°, 35.68°, 43.20°, 53.62°, 57.40° and 62.96° which can be allocated to the (220), (311), (400), (422), (511) and (440) planes, respectively. The FT-IR spectrum showed that the related characteristic peaks of Fe₃O₄ and Fe₃O₄@PPy are similar to a previous study in our lab (Fig. S2). The absorption band at 582 cm⁻¹ was caused by the stretching vibration of the Fe-O bond. The peaks at 794 cm⁻¹ and 890 cm⁻¹ are attributed to the out-of-plane vibration of the C-H. 1033 cm⁻¹ belongs to the typical stretching vibration of the C-N bond in pyrrole. The band at 1299 cm⁻¹ is related to the in-plane vibration of the C-H bond. The basic C=C stretching of the Py ring is situated at 1407 cm⁻¹ and 1544 cm⁻¹, and the appearance of the peak at 1626 cm⁻¹ is attributed to the slight over oxidation of PPy. All the results suggest that PPy was successfully coated on the Fe₃O₄.

3.3. Optimization of MSPE

To obtain a better extraction efficiency, the main parameters of MSPE, including sample pH, adsorption and desorption conditions, were optimized by one-at-a-time optimization strategy. The concentration of 2.0 ng mL⁻¹ was used to optimize the MSPE under different conditions.

3.3.1. Sample pH. Sample solution pH is an essential factor in MSPE methods, which can affect the adsorption efficiency by changing the surface charges of magnetic materials and target compounds. For the universality of this method, the pH of

![Fig. 3 Effect of sample solution pH on extraction efficiency of Fe₃O₄@PPy.](image-url)
surface water samples was optimized. The effect on adsorption capacity of pH in the range of 3–10 was investigated. As it can be seen in Fig. 3, the recoveries of the analytes increased with the pH from 3.0 to 8.0. The analytes retained on Fe3O4@PPy were based on π–π interactions, hydrogen bonding interactions, and hydrophobic. Therefore, pH 8.0 was eventually selected for subsequent study.

3.3.2. Adsorption conditions. The dosage of MNPs, extraction time and temperature as important factors of adsorption conditions were optimized in detail. Firstly, the dosage of Fe3O4@PPy range from 1.0 mg to 20.0 mg was investigated. The results (Fig. 4a) showed a significant increase in extraction efficiency from 1.0 mg to 5.0 mg, and stabilized at 10.0 mg. Therefore, 10.0 mg was selected for subsequent experiment. Furthermore, the adsorption efficiencies from 0 min to 30 min were studied at the same oscillation frequency. Fig. 4b showed that the adsorption of analytes by Fe3O4@PPy increased significantly at 5 min and reached a saturated state at 20 min. So, 20 min was selected as the extraction time of this experiment. In addition, the extraction temperature was optimized, and the data showed that the temperature had little effect on the extraction efficiency, accordingly 25 °C was selected for subsequent analysis (Fig. S3†).

3.3.3. Desorption conditions. To reach a satisfactory elution effect, desorption conditions were needed to be optimized in detail. Firstly, the desorption capability of two solvents, acetonitrile and methanol, were evaluated in different volumes. As shown in Fig. 5a and b, 1.0 mL methanol as the eluent shows higher extraction efficiency than acetonitrile for analytes. Otherwise, the more amount of eluent was used, the longer time was prolonged by nitrogen blowing. Next, the elution time, which is the time of vortex following the addition of the eluent to the adsorbent, was further evaluated. The recoveries of analytes were investigated from 0.5 to 5.5 min. The results indicated that the most target analytes recoveries...
reached maximum values at 1.5 min (Fig. 6). In conclusion, analytes-Fe₃O₄@PPy were eluted with 1.0 mL methanol at room temperature for 1.5 minutes as desorption conditions for MSPE.

### 3.5. Matrix effect and method validation

The matrix effect, linearity range, accuracy, limits of detection (LODs) and quantification (LOQs) of the developed method were evaluated under optimum conditions.

The matrix effect occurs when molecules co-eluting with the compounds of interest alter the ionization efficiency of the electrospray interface.⁴⁴,⁴⁵ Bonfagio et al. reported that the chemical nature of compounds has a significant effect on the matrix effect degree.⁴⁶ Urban surface water has some pollution pathways, such as industrial wastewater, agricultural irrigation and domestic sewage.⁴⁷ There are many potential matrix interferences in surface water, and it is necessary to evaluate the matrix effect of the sample. In this study, the matrix effect was evaluated by the ratio of the response value of the mixed standard solution (B) and the blank spiked sample solution (A), that is, ME (%) = A/B × 100%. The ME between 80% and 120% indicated no obvious matrix effect, while out of the range 80–120% showed significant matrix effect.⁴⁸ The results (Table S3†) showed that the matrix produced inhibitory effects on TCS.

### 3.4. Reusability of Fe₃O₄@PPy

The recycling of Fe₃O₄@PPy was evaluated by recovery of all analytes after multiple extractions. Fe₃O₄@PPy was rinsed with methanol (8.0 mL) and ultrapure water (2 mL) for several times between each test and dried under the same conditions for 5 h. The extraction efficiency of MNPs decreased rapidly after the six recycling. This may be due to the PPy shell of the adsorbent was lost after repeated use and lead to incomplete absorption of the analytes. It turned out that the Fe₃O₄@PPy could be reused for at least six times without a significant loss of the extraction efficiency, indicating the as-prepared Fe₃O₄@PPy owned good stability during the MSPE.

### Table 2 The method validation of MSPE-HPLC-MS/MS

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Linear range (μg L⁻¹)</th>
<th>Calibration equation</th>
<th>LOD (μg L⁻¹)</th>
<th>LOQ (μg L⁻¹)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lower</td>
<td>Mid</td>
<td>Upper</td>
<td>Lower</td>
</tr>
<tr>
<td>PCMP</td>
<td>5.0–1000.0</td>
<td>y² = 211.02x² + 659.62</td>
<td>0.9997</td>
<td>2.0</td>
<td>5.0</td>
<td>86.51</td>
</tr>
<tr>
<td>C12-BAC</td>
<td>0.5–100.0</td>
<td>y = 1.99 × 105x + 2317.07</td>
<td>0.9999</td>
<td>0.2</td>
<td>0.5</td>
<td>92.38</td>
</tr>
<tr>
<td>BAB</td>
<td>0.5–100.0</td>
<td>y = 1.58 × 104x + 5067.95</td>
<td>0.9998</td>
<td>0.2</td>
<td>0.5</td>
<td>84.95</td>
</tr>
<tr>
<td>BEC</td>
<td>1.0–200.0</td>
<td>y = 5.89 × 104x + 2496.74</td>
<td>0.9998</td>
<td>0.3</td>
<td>1.2</td>
<td>97.24</td>
</tr>
<tr>
<td>C14-BAC</td>
<td>0.5–100.0</td>
<td>y = 2.15 × 105x + 1773.17</td>
<td>0.9999</td>
<td>0.2</td>
<td>0.5</td>
<td>95.09</td>
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<tr>
<td>TCC</td>
<td>2.0–1000.0</td>
<td>y = 6162.60x + 1970.62</td>
<td>0.9999</td>
<td>0.5</td>
<td>2.0</td>
<td>100.48</td>
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<tr>
<td>TCS</td>
<td>5.0–1000.0</td>
<td>y = 4347.0x + 1566.10</td>
<td>0.9999</td>
<td>2.0</td>
<td>5.0</td>
<td>101.83</td>
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<tr>
<td>CFC</td>
<td>1.0–500.0</td>
<td>y = 2.30 × 104x + 1311.18</td>
<td>0.9998</td>
<td>0.2</td>
<td>0.5</td>
<td>83.76</td>
</tr>
<tr>
<td>BCP</td>
<td>2.0–1000.0</td>
<td>y = 9665.8x + 1253.54</td>
<td>0.9996</td>
<td>0.5</td>
<td>2.0</td>
<td>85.34</td>
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<tr>
<td>C15-BAC</td>
<td>0.5–100.0</td>
<td>y = 3.69 × 105x + 1026.03</td>
<td>0.9999</td>
<td>0.2</td>
<td>0.5</td>
<td>92.22</td>
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<tr>
<td>HCP</td>
<td>5.0–1000.0</td>
<td>y = 1054.78x + 1020.23</td>
<td>0.9996</td>
<td>2.0</td>
<td>5.0</td>
<td>96.33</td>
</tr>
</tbody>
</table>

- Peak area of the analytes.  
- Concentration of the analytes.

### Table 3 Determination of 11 antiseptic ingredients in real water samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>January</th>
<th>February</th>
<th>March</th>
<th>April</th>
<th>May</th>
<th>June</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAB</td>
<td>d.</td>
<td>0.32/FE3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>TCC</td>
<td>d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>3.07/AP2</td>
<td>2.13/MY2</td>
<td>d.</td>
</tr>
</tbody>
</table>

- Not detected.  
- The average detected concentration is higher than LOD but lower than LOQ.
PCMP, HCP and BCP. Hence, the matrix-matched calibration curves were used to obtain accurate quantitative results. The results of proposed method are tabulated in Table 2 and showed that the MSPE-HPLC-MS/MS method exhibited excellent linearity for all the analytes with correlation coefficients (r) higher than 0.9996. The calculation of LODs and LOQs based on a signal-to-noise ratio of 3 and 10 for analytes were between 0.20–2.0 µg L⁻¹ and 0.50–5.0 µg L⁻¹, respectively. Furthermore, the accuracy was evaluated by recovery and relative standard deviation (RSD). Three spiked concentration were studied in the accuracy was evaluated by recovery and relative standard deviation (RSD). Three spiked concentration were studied in the accuracy.

Table 4 Comparison of the developed method with other methods

<table>
<thead>
<tr>
<th>Extraction method</th>
<th>Analytical method</th>
<th>Sample volume (mL)</th>
<th>Matrix</th>
<th>Recovery (%)</th>
<th>LOD (µg L⁻¹)</th>
<th>LOQ (µg L⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLB</td>
<td>UHPLC-MS/MS</td>
<td>100</td>
<td>Influent of STP²</td>
<td>39–85</td>
<td>0.01</td>
<td>0.05</td>
<td>20</td>
</tr>
<tr>
<td>250</td>
<td></td>
<td></td>
<td>Effluent of STP²</td>
<td>67–92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP-18</td>
<td>GC-MS</td>
<td>500</td>
<td>River water</td>
<td>89–104</td>
<td><em>b</em></td>
<td><em>b</em></td>
<td>21</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>Sewage effluent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>GC-MS</td>
<td>10</td>
<td>Waste water</td>
<td>71.9–86.7</td>
<td>0.13</td>
<td>0.42</td>
<td>49</td>
</tr>
<tr>
<td>MSPE</td>
<td>HPLC-ESI-MS/MS</td>
<td>11 analytes 10</td>
<td>Surface water</td>
<td>80.21–105.80</td>
<td>0.2–2.0</td>
<td>0.5–5.0</td>
<td>This study</td>
</tr>
</tbody>
</table>

⁰ Sewage treatment plant. _b_ — not mentioned.

3.6. Analysis of real water samples

The established MSPE-HPLC-MS/MS method was used to extract and detect 11 antiseptic ingredients in 18 surface water samples. The samples were collected from three regions along the Hutuo River (from south to north in Gaocheng, Shijiazhuan and Zhengding) for six consecutive months. As shown in Table 3, the detected results of BAB showed an upward trend from February to May, meanwhile, the concentration of BEC gradually increased from March to June. TCC had the highest level in April owing to the frequency use of personal cleaning during the outbreak. All the results were closely related to the massive use of cleaning and disinfection products during the COVID-19 epidemic. With the spread of the epidemic, the disinfection of public and personal living environments increased in urban and rural areas. Therefore, the content of antiseptic ingredients in surface water increased gradually, which could be explained.

3.7. Method comparison

In this study, 11 antiseptic ingredients, including phenols, ureas and QACs, were tested. In preliminary experiment, C18 cartridge and HLB cartridge were used for sample pretreatment, and the results showed that the recoveries of these two methods were lower than the MSPE method. The GC-MS method had some advantages in the detection of volatile substances. However, some antiseptic ingredients have poor volatility, which were more suitable for the detection of LC-MS. In this study, the HPLC-ESI-MS/MS technology, which had a wide range of applications, was used to detect multiple types of antiseptic ingredients simultaneously. Compared with previous UHPLC-MS/MS study, more antiseptic ingredients were detected.

Characteristics of the developed method were compared with other SPE methods reported for the purification and determination of antiseptic ingredients from water. The comparison of sample volume, recovery, LODs, and LOQs were listed in Table 4. According to the results, the proposed method had some advantages in sample volume, recovery, LOD, and LOQ. In this study, less sample volume was needed, and desirable recovery was received based on the high-surface contact area between MNPs and analytes. Moreover, the proposed method also had lower LODs and lower LOQs attributing to the excellent extraction efficiency. Compared with SPE column methods, small amount of elution solvent was needed, which was environmentally friendly method. In addition, the MSPE technology could avoid packing of Fe₃O₄@PPy composite into the cartridge, column blocking and high pressure, which often suffered in SPE. Extraction time of the method was 20 min, which was usually shorter than column separation method. MSPE employed an external magnetic field to extract analytes efficiently, simplifying the extraction process. Furthermore, Fe₃O₄@PPy adsorbent could reused easily, which
was economical. In general, the developed method showed advantages of simplicity, rapidity, efficiency, and environment friendliness.

4. Conclusion
In present study, Fe$_3$O$_4$@PPy was synthesized by a simple and efficient chemical oxidative polymerization method and further used for the extraction of 11 antiseptic ingredients in surface water. The Fe$_3$O$_4$@PPy had excellent stability and reusability, in addition, it showed satisfactory adsorption capacity for the analytes. The method validation demonstrated that the MSPE-HPLC-MS/MS showed desirable linearity, and accuracy as well as low LODs and LOQs. As a whole, the established method showed excellent advantages in extraction and determination of antiseptic ingredients in real sample as well as provided a new strategy to monitor antiseptic ingredients in surface water during the COVID-19 epidemic.

Conflicts of interest
There are no conflicts to declare.

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References


