Implementation of an automatic and miniature on-line multi-parameter water quality monitoring system and experimental determination of chemical oxygen demand and ammonia-nitrogen

Yingke Xie, Zhiyu Wen, Zhihong Mo, Zhiqiang Yu and Kanglin Wei

ABSTRACT

An automatic, miniature and multi-parameter on-line water quality monitoring system based on a micro-spectrometer is designed and implemented. The system is integrated with the flow-batch analysis and spectrophotometric detection method. The effectiveness of the system is tested by measuring chemical oxygen demand (COD) and ammonia-nitrogen in water. The results show that the modified system provides a cost-effective, sensitive, reproducible and reliable way to measure COD and ammonia-nitrogen in water samples with automatic operation and low toxic chemical consumption. In addition, the experiment results show that the relative error of the system is less than 10%, the limit of detection is 2 mg/L COD and 0.032 mg/L ammonia-nitrogen, respectively, and the relative standard deviation was 6.6% at 15.0 mg/L COD ($n = 7$) and 5.0% at 0.300 mg/L ammonia-nitrogen ($n = 7$). Results from the newly designed system are consistent with the data collected through the Chinese national standard analysis methods.

Key words | absorbance, ammonia-nitrogen, chemical oxygen demand, micro-spectrometer, on-line, water quality monitoring

ABBREVIATIONS

COD | chemical oxygen demand
DC | direct current
NSPRC | National Standard of the People’s Republic of China
LOD | limit of detection
RSD | relative standard deviation
SD | standard deviation
HC | holding coil
MV | multiposition valve

INTRODUCTION

Water quality monitoring can provide early warnings of water pollution and help people choose the correct way to protect water resource (Storey et al. 2011; Hou et al. 2013). It has been estimated that on-line monitoring for real-time processing may save as much as 40% of the energy currently needed for wastewater treatment (Qin et al. 2012). As water resource protection has become a global issue, water quality monitoring is now a subject of growing importance.

Conventional water quality monitoring in the laboratory has advantages of accuracy, good reproducibility and simple instrumentation, but accuracy also depends on the operator’s skills and the result lacks timeliness (Almeida et al. 2012). Comparatively, automatic on-line water quality monitoring systems can minimize these drawbacks. Most current automatic monitoring systems are single-parameter systems, and their complicated structure, large size and high cost do not meet the current requirements for water quality monitoring (Olsson et al. 2007; Chen et al. 2011; Kröckel et al. 2011; Almeida et al. 2012; Tew et al. 2014). Consequently, we see there are three trends in improving water quality monitoring systems in recent years: (a) automation, (b) miniaturization and (c) multi-parameter (Andruch et al. 2012; Banna et al. 2014).

To some extent, the flow-batch analysis (FBA) with the spectrophotometric detection method can fulfill objectives discussed above. The FBA system is a flow-based analytical
system, which provides automatic sample preparation and detection (Diniz et al. 2012). In this system, the sampling step and the sample/reagents transportation are done in the same way as in a flow analyzer, whereas mixing and reaction are performed inside a mixing chamber as in a batch system. The sample aliquot is maintained in one chamber during the entire process, to minimize dispersion and preserve sample identity (Honorato et al. 2001; Khanhuathon et al. 2013). Moreover, the spectrophotometric detection method based on a micro-spectrometer can detect the continuous spectrum and minimize the size of the monitoring system.

Compared with other water quality parameters, chemical oxygen demand (COD) and ammonia-nitrogen are more significant, especially in characterizing industrial wastewater pollution and drinking water source quality (Ray et al. 2014; Yu et al. 2015). In China, the 1st National Census of Pollution Sources (NCPS) showed the actual emissions of COD and ammonia-nitrogen are 30 million tons and 1.79 million tons, respectively, which greatly exceed national environmental capacity of 7.4 million tons for COD and 0.5 million tons for ammonia-nitrogen. Consequently, the real-time COD and ammonia-nitrogen monitoring, especially the monitoring in sewage treatment plant and source water, are of great importance for our living life. However, the conventional methods of COD measurement require high temperature and high pressure for digestion, which result in complicated and bulky equipment, reagents with high cost and toxicity, and serious secondary pollution (Almeida et al. 2012). Comparatively, using Fenton reagents for COD determination could digest water sample on-line under normal temperature and pressure, which requires simple equipment and leads to less secondary pollution (Lee & von 2010; Real et al. 2010; Mei & Rosario-Ortiz 2012).

Based on the factors mentioned above, an automatic and miniature on-line multi-parameter water quality monitoring system based on FBA and a micro-spectrometer was developed. In addition, the effectiveness of the system has been tested by determining COD and ammonia-nitrogen in water. Also the results collected by different systems (the proposed system and Chinese national standard analysis methods) from the same water sample were compared and evaluated.

**METHODS**

**Principle**

In this experiment, we use Fenton reagents (H₂O₂ and FeSO₄) as digestion reagents for the determination of COD, and high temperature, high pressure and strong acids are needless. The principle is as Equation (1) (Lee & von 2010; Real et al. 2010; Mei & Rosario-Ortiz 2012), where OC is the abbreviation for organic compounds.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\cdot\text{OH} + \text{OC} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot\text{HO}_2 + \text{H}^+
\end{align*}
\]

However, throughout the whole reaction process, there is no spectral change; so the spectrophotometric detection method cannot be used to measure COD. In order to solve this problem, we use malachite green as a chromogenic reagent in the experiment. Malachite green is a green alkaline organic dye that can be digested by the hydroxyl radical (·OH), and it has a characteristic absorption peak at 610 nm that can be detected by a spectrometer. In mixed solutions, the organic compounds and malachite green will compete to consume ·OH. As organic compounds have higher affinity to ·OH than malachite green, the more COD in water, the more malachite green residue is left, resulting in higher absorbance at 610 nm. Therefore, the ΔA can be detected by spectrometer (ΔA = A₀ − Aₙ₀). A₀ and A are the absorbance at 610 nm before and after reaction, respectively. The linear relationship between the concentration of COD in water and the absorbance of the remaining malachite green reagent allows the calculation of COD concentration in water.

According to National Standard of the People’s Republic of China (NSPRC) HJ536-2009, the principle of determining ammonia-nitrogen is as follows: in alkaline medium (pH = 11.7) and with the existence of sodium nitriferricyanide, ammonia and ammonium ions in water can react with salicylate and hypochlorite, and then produce a blue compound with a characteristic absorptive wavelength at 697 nm. Therefore, the content of ammonia-nitrogen in water can be determined by measuring the absorbance at 697 nm.

**Reagents and standard solutions**

In this experiment, all chemicals used were of analytical reagent grade and all solutions were prepared with deionized water.

To measure COD, FeSO₄ and H₂O₂ were used as digestion reagents and malachite green was used as chromogenic reagent. A 37.5 mmol/L FeSO₄ solution (pH 2.0) was prepared by dissolving 0.0834 g FeSO₄ in 1,000 mL deionized water to which 0.28 mL concentrated sulfuric acid was
A 90 mmol/L H₂O₂ solution was prepared by diluting 0.61 mL 30% H₂O₂ solution to 1,000 mL with deionized water. A 100 mol/L malachite green solution was prepared by dissolving 0.0365 g malachite green in deionized water and diluting to 1,000 mL. The COD standard solution was prepared daily from a stock made by dissolving 0.0319 g potassium hydrogen phthalate in 1,000 mL deionized water to make a 37.5 mg/L stock solution (potassium hydrogen phthalate is a reducing organic compound which is difficult to digest, often used as a COD standard solution in water quality determination).

To measure ammonia-nitrogen, a sodium salicylate solution was prepared by dissolving 58 g sodium salicylate, 50 g potassium sodium tartrate and 5.0 g sodium nitroprusside in deionized water and diluting to 1,000 mL, and a sodium hypochlorite solution was prepared by dissolving 10 mL sodium hypochlorite and 66 g sodium hydroxide in deionized water and diluting to 1,000 mL. The ammonia-nitrogen standard solution was prepared daily from diluting a 100× stock to make a 0.500 mg/L stock solution, and the 100× stock was made by dissolving 190.9 mg ammonium chloride in deionized water and diluting to 1,000 mL.

**System setup**

Figure 1 shows the schematic of the system setup. It consists of a 5.0 mL syringe pump MSP1-C2 (Baoding Longer Precision Pump, Baoding, Hebei, China) and a 12-port multiposition valve (MV) (Valco Instrument, Houston, TX, USA). A holding coil (HC) (PTFE tubing, 1 mm i.d., 7 m long, VICI, USA) and PTFE tubing (1 mm i.d.) were connected to the ports of the MV. A mixing chamber was employed for mixing in the reaction zone. A halogen tungsten lamp (5 W) collimated by a planoconvex lens (74-VIS, Oceanoptics, USA) was used as light source and a visible (VIS) spectrophotometer MSVIS-2 (Chongqing University, Chongqing, China) was used for spectrophotometric determination.

Figure 2(a) shows the front view of the mixing chamber used in the system, and Figure 2(b) shows the side view. A cuvette (quartz, 20 mm path length, 4 mL internal volume) is surrounded by a water bath. The digestion reaction and chromogenic reaction take place in the cuvette and are accelerated by air-agitation. An ultrasonic transducer (10 W, 40 KHz) is controlled by an ultrasonicator to assist digestion and cuvette cleaning. The temperature of the water bath (±0.1°C) is adjusted by Peltier elements through a temperature sensor. After passing through the cuvette, the detection parallel light is coupled into a fiber through a planoconvex lens (74-VIS, Oceanoptics, USA) and then is sent to a micro-spectrometer. Figure 2(c) shows the cuvette we used in the system. Two pipes at the bottom of cuvette are connected to a direct current (DC) electromagnetic pump for air-agitation and liquid discharge, respectively.
According to the Lambert–Beer law (Dennison et al. 1993), if the light path is fixed, the concentration \( C \) is proportional to the absorbance \( A (=\lg(I/I_0)) \), \( I \) is the intensity of the incident light and \( I_0 \) is the intensity of the emergent light). In the system, a micro-spectrometer (Figure 2(d)) with a dimension of 88 mm \( \times \) 78 mm \( \times \) 42 mm is used to detect the optical spectra and compute light intensity. The micro-spectrometer was developed by Microsystem Center of Chongqing University independently. With a wavelength resolution around 2 nm, it allows the researcher to capture and transfer the full spectrum from 350 to 780 nm.

**Procedure**

Based on a Raspberry Pi (Model B+) computer board and home-made expansion boards, human–computer interaction software written in C/C++, runs on the embedded Linux operating system to realize system control, automatic operation and spectral data processing.

Before running the operational sequence, the HC and the tubing connecting to port 3 of the MV were filled with deionized water. Tubing connected to other ports of the MV were filled with their respective solutions, except for port 1 where the tubing was filled with air before connecting it to the mixing chamber.

The procedure begins with the syringe pump in the valve-in position, where 2.0 mL of deionized water is aspirated at 200 \( \mu \)L/s. After changing the pump to the valve-out position, 0.2 mL air is aspirated into HC to separate the deionized water from the following solutions. For determination of COD, the water sample or standard solution is aspirated into HC through port 12 of the MV and then injected into the cuvette through port 1 at 120 \( \mu \)L/s. Next, 0.2 mL FeSO\(_4\) solution, 0.2 mL air (separate the FeSO\(_4\) solution from H\(_2\)O\(_2\) solution in HC) and 0.2 mL H\(_2\)O\(_2\) solution are aspirated into HC sequentially through port 9, port 2 and port 10 of the MV, respectively, and then are injected into the cuvette through port 1 at 120 \( \mu \)L/s. Then, the ultrasonication assists digestion under normal temperatures (26.5°C) and normal pressures (atmospheric pressure) for 15 minutes by controlling the switching time of the ultrasonicator. After that, 0.6 mL malachite green solution is aspirated into HC through port 11 of the MV and then injected into the cuvette through port 1 at 120 \( \mu \)L/s, and air-agitation works for 1 minute to accelerate the chromogenic reaction by controlling the switching time of the DC electromagnetic pump. Finally, after the solution is left to stand for 3 minutes, the spectrum is detected by the micro-spectrometer.

Similarly, for determination of ammonia-nitrogen, a 2.0 mL water sample or standard solution is aspirated into HC through port 12 of the MV and then injected into the cuvette through port 1 at 120 \( \mu \)L/s. Next, 0.2 mL sodium salicylate solution, 0.2 mL air and 0.2 mL sodium hypochlorite solution are aspirated into HC sequentially through port 6, port 2 and port 7 of the MV, respectively, and then are injected into the cuvette through port 1 at 120 \( \mu \)L/s.

---

**Figure 2** | (a) The front view of mixing chamber. (b) The side view of mixing chamber. (c) The cuvette used in the system. (d) The micro-spectrometer used in the system.
air-agitation works for 5 minutes to accelerate the reaction. Finally, after solution is left to stand for 1 minute, the spectrum is detected by the micro-spectrometer.

RESULT AND DISCUSSION

Effect of air-agitation on optical detection system

The interference of air-agitation to the optical detection system has been investigated. Figure 3 shows the correlation between the intensity of deionized water and the frequency of air-agitation switch on and off at different wavelengths. The intensity is detected by the micro-spectrometer and the time interval between each measurement is 1 s. In Figure 3, the times (×) of 28 to 43 and 135 to 165 represent air-agitation is on, and the others represent air-agitation is off. Curve a, b, c, d, e and f in Figure 3 correspond to wavelength 410.11, 445.02, 515.17, 560.02, 642.15 and 710.10 nm, respectively, which cover the spectrum range of the micro-spectrometer. It is clear that intensity fluctuates when air-agitation is on and stabilizes quickly when air-agitation is off. That is to say, there is no obvious interference to optic measurement when the solution stands for some time after air-agitation.

Optimization of system cleaning

The interplay among reagents used for different parameters is the major cause of error in multi-parameter monitoring. We have adopted methods to reduce error. (1) PEEK tubing is used throughout the system due to its corrosion resistance, high-purity, high-strength, wear resistance and high temperature endurance property. (2) The reagents and water sample only flow through MV, HC and the cuvette; the syringe pump is not contaminated. (3) To clean HC, the running speed of the syringe pump can be increased to 1,000 μL/s to generate a high-pressure water jet, and the clean water is directly discharged through port 8 of the MV without polluting the cuvette. (4) To clean the cuvette, we use ultrasound-assistance and air-agitation to improve cleaning efficiency. Considering the cavitation effect of ultrasonication is optimal when temperature is at 30–40 °C, the water bath is heated to 35 °C by Peltier elements during cuvette cleaning.

To test the cleaning effect, we use methylene blue (an active organic reagent) to pollute the system, especially the HC and cuvette. The absorbance of discharged water was then measured by a UV-Vis spectrophotometer, UV-2450 (Shimadzu, Japan). Figure 4(a) shows the absorbance
spectrum of methylene blue. Figure 4(b) shows the overlapping absorbance spectra of HC discharge water after HC was cleaned with 10 mL, 15 mL and 20 mL deionized water, respectively. Figure 4(c) shows the absorbance spectrum of cuvette discharge water after 2.5 minutes cuvette cleaning at the temperature of 35°C with ultrasound-assistance and air-agitation. In Figure 4(b) and 4(c), the full curve is the absorbance spectrum of deionized water. After HC was cleaned with 20 mL deionized water and the cuvette was cleaned with ultrasound-assistance and air-agitation, the absorbance at 662 nm (the characteristic absorptive wavelength of methylene blue) was reduced to 0, close to the absorbance of deionized water, which indicates the system has been cleaned.

**Determination of COD and ammonia-nitrogen**

**Calibration curve and spectral analysis**

The calibration curves are set up automatically. Through on-line operation, 0, 0.20, 0.40, 0.80 and 1.20 mL COD standard solutions are injected into the cuvette and then diluted with 2.00, 1.80, 1.60, 1.20 and 0.80 mL deionized water, corresponding to COD concentration 0, 3.75, 7.5, 15 and 22.5 mg/L, respectively. Air-agitation works for 15 s to mix the solutions.

Figure 5(a) shows the overlapping spectra of the solution (between 400 and 750 nm) after reaction with different COD concentration. It is clear that the absorbance at 610 nm (the characteristic absorption wavelength of malachite green) increases with higher COD concentration, but hardly changes at 610 nm and 680 nm. Therefore, 610 nm and 680 nm are considered as characteristics of the background interference and are used as reference wavelength. To correlate the absorbance value and corresponding standard solution concentration, the three-wavelength spectrophotometry method was used as shown in Equation (2).

\[
\Delta A_{COD} = A_{610} - 0.35A_{480} - 0.65A_{680} = kC_{COD}
\]

where \(A_{610}, A_{480} \) and \(A_{680} \) are the absorbance measured at wavelength 610, 480 and 680 nm, respectively, \(C_{COD} \) is the concentration of COD and \(k \) is the proportionality coefficient. Proportionality coefficient 0.35 is calculated through \((680 - 610)/(680 - 480)\) and 0.65 is calculated through \((610 - 480)/(680 - 480)\).

Figure 5(b) shows the correlation between absorbance value \(A (=A_{COD} - A_{blank}, A_{blank} \) is the absorbance of blank calculated by Equation (2)) and COD concentration (mg/L), where the straight line linking each two points is obtained according to the least squares theory, and the slope of the line indicates the magnitude of \(k \) in Equation (2). The error bar is the standard deviation (SD) of repeating measurements for five times. According to the correlation coefficient \(R^2 = 0.9987 > 0.9900\), the calibration curve is credible.

Similarly, through on-line operation, 0, 0.20, 0.40, 0.80 and 1.20 mL ammonia-nitrogen standard solution are injected into the cuvette, and diluted with 2.00, 1.80, 1.60, 1.20 and 0.80 mL deionized water, corresponding to ammonia-nitrogen concentration 0, 0.075, 0.15, 0.3 and 0.5 mg/L, respectively. Air-agitation worked for 15 s to mix solutions.

Figure 6(a) shows the overlapping spectra with different ammonia-nitrogen concentration. It can be seen that the absorbance at 697 nm (the characteristic absorption wavelength of blue compound) increases with higher ammonia-nitrogen concentration. For the limit of the wavelength range of the micro-spectrometer, one reference wavelength at 550 nm was chosen and the two-wavelength
The spectrophotometry method (Equation (3)) was used to process spectral data.

\[ \Delta A_{AN} = A_{697} - A_{535} = kC_{AN} \]  

(3)

where \( A_{697} \) and \( A_{535} \) are the absorbance measured at wavelength 697 nm and 535 nm, respectively, \( C_{AN} \) is the concentration of ammonia-nitrogen and \( k \) is the proportionality coefficient.

Figure 6(b) shows the correlation between absorbance value \( A \) (=\( A_{AN} \) - \( A_{blank} \), \( A_{blank} \) is the absorbance of blank calculated by Equation (3)) and ammonia-nitrogen concentration (mg/L), where the straight line linking each two points is obtained according to the least squares theory, and the slope of the line indicates the magnitude of \( k \) in Equation (3). The error bar is the SD of repeating measurements for five times. According to \( R^2 = 0.9994 > 0.9990 \), the calibration curve is credible.

**Accuracy and reproducibility**

The different concentrations of COD and ammonia-nitrogen standard water samples were analyzed by the proposed system. The standard water samples (potassium hydrogen phthalate solution and ammonium chloride solution) were prepared in a laboratory of Chongqing University according to the Chinese national standard. Each determination uses 2 mL standard sample, and after the digestion and chromogenic reaction the spectrum is detected and the concentration is calculated by the previously established calibration curve.

Part of the experimental results are shown in Table 1. The recovery rates of COD and ammonia-nitrogen are in the ranges of 91.2%–108.8% and 93.8%–106.8%, respectively, representing good accuracy.

Moreover, the same standard water sample was repeatedly tested in equal precision measurement, and the relative standard deviation (RSD) was calculated according to Equation (4) (Clinch et al. 1987).

\[
\text{RSD} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (C_i - \bar{C})^2 / \bar{C}}
\]  

(4)

where \( n \) is the number of measurements, \( C_i \) is the concentration of \( i \)th measurement, and \( \bar{C} \) is the average concentration of all measurements. The results show that

### Table 1 | Part of the experimental results for determination of standard water samples (\( n = 5 \))

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>COD Standard sample values (mg/L)</th>
<th>Experimentally measured values (mg/L)</th>
<th>Recovery (%)</th>
<th>Ammonia-nitrogen Standard sample values (mg/L)</th>
<th>Experimentally measured values (mg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0</td>
<td>5.1 ± 0.3</td>
<td>102.4 ± 6.0</td>
<td>0.100</td>
<td>0.101 ± 0.007</td>
<td>102.0 ± 6.8</td>
</tr>
<tr>
<td>2</td>
<td>7.5</td>
<td>7.6 ± 0.6</td>
<td>101.9 ± 6.9</td>
<td>0.150</td>
<td>0.147 ± 0.006</td>
<td>97.9 ± 4.1</td>
</tr>
<tr>
<td>3</td>
<td>10.0</td>
<td>10.0 ± 0.7</td>
<td>100.4 ± 6.3</td>
<td>0.200</td>
<td>0.204 ± 0.008</td>
<td>102.2 ± 3.9</td>
</tr>
<tr>
<td>4</td>
<td>15.0</td>
<td>15.2 ± 0.8</td>
<td>101.2 ± 5.4</td>
<td>0.500</td>
<td>0.306 ± 0.010</td>
<td>102.1 ± 3.5</td>
</tr>
<tr>
<td>5</td>
<td>20.0</td>
<td>19.6 ± 1.4</td>
<td>98.1 ± 6.9</td>
<td>0.500</td>
<td>0.499 ± 0.019</td>
<td>99.8 ± 3.9</td>
</tr>
<tr>
<td>6</td>
<td>24.5</td>
<td>24.1 ± 1.0</td>
<td>98.2 ± 4.1</td>
<td>0.700</td>
<td>0.715 ± 0.021</td>
<td>102.1 ± 3.0</td>
</tr>
</tbody>
</table>
the system has a precision of 6.6% RSD at 15.0 mg/L COD ($n = 7$) and 5.0% RSD at 0.300 mg/L ammonia-nitrogen ($n = 7$), representing good reproducibility.

**Sensitivity**

The sensitivity is defined as the ratio of the absorbance with the corresponding concentration of the measured parameter. Therefore, the sensitivity is equal to the slope value of the calibration curve. It can be seen from Figure 5(b) and Figure 6(b) that the sensitivity for determination of COD and ammonia-nitrogen is 0.0208 and 1.46, respectively.

**Limit of detection**

According to Equation (5) (Derouiche et al. 2007), the calculated limit of detection (LOD) was 2 mg/L COD and 0.032 mg/L ammonia-nitrogen, respectively.

$$LOD = \frac{3S_b}{k}$$  

(5)

where $S_b$ is the SD of blank absorbance measurements calculated by the Bessel formula ($n = 5$) and $k$ is the sensitivity.

**Linear measuring range**

The linear measuring range of the system meets the monitoring requirements for class I, class II and class III surface water quality standards (NSPRC GB3838-2002). To measure samples with higher concentration of COD and ammonia-nitrogen, we can dilute water samples with deionized water before analyzing according to Equation (6) (NSPRC HJ/T 399-2007 and NSPRC HJ536-2009).

$$C = \frac{A_s - A_b - a}{k} \times D$$  

(6)

where $C$ is the concentration of COD or ammonia-nitrogen (mg/L), $A_s$ is the calculated absorbance of mixing solution, $A_b$ is blank absorbance, $a$ is the intercept of the calculated curve, $k$ is the slope of the calculated curve and $D$ is the dilution ratio.

**Determination of real water samples**

Real water samples of treated effluent water were collected from a sewage treatment plant in Beibei, Chongqing, China. Each determination used 2 mL real water sample. As shown in Table 2, the COD and ammonium-nitrogen values of real water samples were obtained using the proposed system and compared with those obtained using the Chinese national standard analysis method (NSPRC HJ/T 399-2007 and NSPRC HJ536-2009). Results indicate that the values were not significantly different between the two systems, and the relative errors are always less than ±10%, showing that the system is accurate.

The most important advantage of the proposed system, compared with the Chinese national standard analysis method, is that the system requires much less measuring time (only a quarter of the time is required) for on-line monitoring of COD at normal temperatures and normal pressures.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>COD</th>
<th>Ammonia-nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>National standard method (mg/L) (A)</td>
<td>Proposed system measured values (mg/L) (B)</td>
</tr>
<tr>
<td>1</td>
<td>16.8</td>
<td>18.1</td>
</tr>
<tr>
<td>2</td>
<td>25.0</td>
<td>23.4</td>
</tr>
<tr>
<td>3</td>
<td>24.2</td>
<td>22.9</td>
</tr>
<tr>
<td>4</td>
<td>18.3</td>
<td>19.1</td>
</tr>
<tr>
<td>5</td>
<td>18.7</td>
<td>19.3</td>
</tr>
<tr>
<td>6</td>
<td>17.1</td>
<td>18.6</td>
</tr>
<tr>
<td>7</td>
<td>25.6</td>
<td>23.7</td>
</tr>
<tr>
<td>8</td>
<td>16.8</td>
<td>18.1</td>
</tr>
</tbody>
</table>

*Number of replicates = 3.

$\%(B - A)/A \times 100%$.

$\%(D - C)/C \times 100%$. 

Table 2 | Results of the contrast experiment for real water samples*
and consumes less power (<50 W) and the whole system size is 650*350*180 mm.

CONCLUSIONS

In summary, an automatic and miniature on-line multi-parameter water quality monitoring system based on a microspectrometer has been investigated and developed, and used to measure COD and ammonia-nitrogen in water. The results show that the modified system provides a cost-effective, sensitive, reproducible and reliable way to measure COD and ammonia-nitrogen in water samples, with automatic operation and low toxic chemical consumption. And the system meets the demands of automation, miniaturization, effectiveness, multi-parameter and less secondary pollution. Meanwhile, experimental results show that the relative error is less than 10%, 6.6% RSD at 15.0 mg/L COD (n = 7) and 5.0% RSD at 0.300 mg/L ammonia-nitrogen (n = 7). In addition, experiment results of the proposed system are consistent with the data collected through Chinese national standard analysis methods. Additionally, in the spectrum range of the micro-spectrometer, more water quality parameters can be tested using the spectrophotometric detection method in the proposed system. In the future research, we plan to use this system to determine COD and ammonia-nitrogen with wider concentrations range, and to measure more water quality parameters. We hope that the results in this paper will be useful to improve the water quality on-line monitoring in the future.

ACKNOWLEDGEMENTS

This work was supported by the China international cooperative project of science and technology (project no. 2007DFC00040).

REFERENCES


First received 7 March 2015; accepted in revised form 6 October 2015. Available online 26 October 2015