Determination of Chemical Oxygen Demand in Water Samples Using Gas-phase Molecular Absorption Spectrometry

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Chemical oxygen demand (COD) is important for water quality assessment as it represents the level of reductive organic pollution from eutrophication in aquatic systems. For surface water quality monitoring, permanganate is usually applied as an oxidizing reagent, and the routine COD_{Mn} determination is mostly achieved by titration method. However, this titration method is tedious and time consuming, and the results suffer from environmental temperature fluctuations and complicated operation techniques. In this study, a novel COD_{Mn} determination method was developed using gas-phase molecular absorption spectrometry equipped with an online automated digestion device for the first time. The effects of digestion temperature, digestion time and sulfuric acid content were thoroughly studied. This method exhibited good linearity (0.35 to 12 mg/L), a low detection limit (0.12 mg/L), and good RSD from various water samples (0.71 – 2.37%). When used for COD_{Mn} determination in routine water quality monitoring, this automated GPMAS can considerably improve analysis speed, efficiency, accuracy and stability compared to the traditional titration method.

Introduction

Chemical oxygen demand (COD) is an important parameter for assessing water quality.[1] This parameter has been widely used to determine the level of water pollution caused by organic pollutants, specifically the reductive fraction of organic pollutants that are responsible for eutrophication in aquatic systems.[2] COD measurement involves determining the number of oxygen equivalents consumed in the oxidation and decomposition of organic compounds in a sample with powerful oxidizing reagents, such as dichromate or permanganate under defined conditions. In China, the permanganate-based method is designated as permanganate index (COD_{Mn}) (GB11892-89) and usually adopted to evaluate reductive pollution levels in surface water (Chinese National Standard GB 3838-2002) and ground water (Chinese National Standard GB/T 14848-2017) with the oxygen demand of organic compounds ranging from 1.0 to 15.0 mg/L.[3]

Conventionally, the COD_{Mn} measurement is achieved by titrimetric analysis standard method, such as International Standard ISO 8467-1993, Japanese Standard JIS K0102, and Chinese Standard GB 11892-89, which is limited by its long digestion time and tedious titration operation. Additionally, the accuracy and precision of results depend largely on the skill of personnel.[4-6] In order to overcome these problems, many efforts have been made to replace this traditional titration method with other techniques that include open/close reflux methods,[3] electrochemical methods,[7,8] spectrophotometric methods,[9] hydrolysis and commercial COD kit analysis methods.[10,11] Also, commercial automatic COD_{Mn} analyzers have been developed, but these instruments are usually expensive to purchase and maintain.[12] Due to the fast analysis speed, easy automation, and low sample and reagent consumption, flow injection analysis has been considered one of the most popular technologies for COD_{Mn} determination.[13] Various improvements to the flow injection analysis system have been reported, including an alternative oxidation method, variation of detection, and online regeneration of consumed oxidizing reagents, to further enhance analysis performance.[14-18] However, flow injection analysis does not follow the principle of current COD_{Mn} standard methods, and possesses some intrinsic drawbacks. Firstly, the flow injection analysis system can only collect and analyze a small fraction of water sample, ignoring substances that are unable to disperse throughout the aqueous phase, such as suspended and precipitated particles, and consequently results in a deterioration in the sampling representativeness. In addition, when dealing with water samples from a mining area, the high content of metal ion in the water sample is likely to react with the carrier solution, causing unexpected color change and disturb spectrophotometric determination.[19] Therefore, it is necessary to develop automated COD_{Mn} determination techniques with high repeatability and accuracy for measuring a large number of samples.

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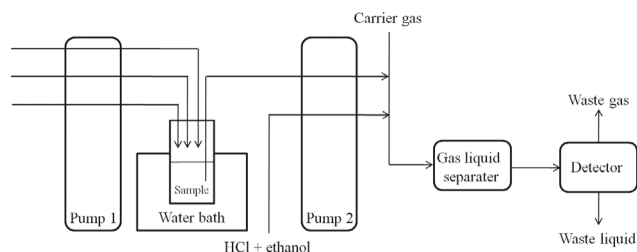E-mail: tli7@swu.edu.cn

Fig. 1   Scheme for determination of COD_{Mn} by GPMAS.

Table 1   Instrumental parameters for gas-phase molecular absorption spectrometer

Working parameter	
Light source	Deuterium lamp
Wavelength	213.9 nm
Light path length	24 cm
Input pressure of nitrogen	0.3 MPa
N_2 flow rate	9 mL/min
Delay time	40 s
Sample pump speed	50.0 rpm
Reagent pump speed	25.0 rpm
Measurement mode	Peak height

Gas phase molecular absorption spectrometry (GPMAS) is an ideal analytical technique for determination of volatiles or analytes that can be easily converted into volatile compounds.[20-22] In GPMAS measurement, analytes are vaporized into the gas phase, and then transported by carrier gas stream into a flow-through absorption cell, where the absorbance signal of the analytes are measured at selected wavelengths. When coupled with an atomic absorption spectrometer detection system, GPMAS has been successfully applied to the determination of ammonium, sulfide, and nitrate.[23-25]   Recently, the UV-Vis spectrophotometer has been introduced as a GPMAS detection system, which allows the researchers to study the analytes spectrum in a wide wavelength range.[26]   This UV-Vis spectrophotometer provides faster analysis speed, simpler operation and more reliable data, which also expands the GPMAS application field to more ions such as arsenic, tin, ammonium, nitrite, nitrate, and sulfite.[27,28] Thus, such a system holds promise for the application of GPMAS for the determination of COD_{Mn}.

In this study, a novel GPMAS method has been developed and applied to determine COD_{Mn} for the first time. This method uses $NaNO_2$ as reduction reagent, and the measurement of COD_{Mn} was achieved using a modified GPMAS instrument. This GPAMS method follows the principles of the current COD_{Mn} standard methods, which involve the oxidation of water sample by $KMnO_4$, addition of excessive reduction reagent ($NaNO_2$), and subsequent determination of excess $NaNO_2$ by GPMAS. This method is an ideal replacement for traditional titration-based COD_{Mn} standard methods.   Critical factors including digestion temperature, digestion time and sulfuric acid concentration were thoroughly investigated and optimized. The analytical performance of the developed GPMAS method was evaluated using critical reference materials (CRMs).   Then, this method was applied to the determination of real water samples and compared to previously FIA-based COD_{Mn} determination methods as well as titration-based COD_{Mn} standard methods. This GPMAS-based COD_{Mn} measurement method was found to provide satisfactory sensitivity, reproducibility and analysis speed, and thus could serve as a high-throughput analytical technique for routine monitoring of COD_{Mn}.

Experimental

Reagents and chemicals

Potassium permanganate, ethanol, sodium hydroxide, sulfuric acid and hydrochloric acid, sodium oxalate, and sodium nitrite were purchased from Sinopharm Chemical Reagent Co., Ltd. The potassium permanganate, sodium hydroxide, sulfuric acid and hydrochloric acid used in the experiment were analytical reagents, ethanol was a guarantee reagent, sodium oxalate was a standard reagent, sodium nitrite was a specpure reagent, and all

solutions were prepared using ultra-high purity water (Elga, >18.2 MΩ·cm).

A stock permanganate solution was prepared by dissolving 3.20 g of $KMnO_4$ in 1200 mL of water. The solution was heated until the volume was reduced to approximately 1000 mL. After cooling and filtering through a 0.45-μm membrane filter, this stock solution was standardised by titration with sodium oxalate solution and stored in the dark.   A 0.0090 – 0.0096 mol/L $KMnO_4$ standard solution was prepared by diluting the stock solution.   A stock sodium oxalate solution was prepared by dissolving 0.6705 g of sodium oxalate ($Na_2C_2O_4$, dried at 105 – 110°C for 2 h) in 100 mL of water.

A stock sodium nitrite solution was produced by dissolving 4.9260 g of sodium nitrite ($NaNO_2$, dried at 105 – 110°C for 2 h) in 1000 mL of water.   A sodium nitrite reaction solution was prepared by diluting 70.0 mL of sodium nitrite stock solution with 1000 mL water.   A HCl/ethanol solution was prepared by mixing 250 mL of hydrochloric acid and 300 mL of ethanol, and diluting to 1000 mL water.   A 1 + 3 (V + V) sulfuric acid solution was obtained by mixing 300 mL of sulfuric acid and 900 mL of water.   The nitrite standard solution (100 mg/L) and the permanganate index standard solution (batch numbers: 170543, 170545, 203165, 160960, 160961, 160962, 203166, 161341, 203164, 203165) were obtained from the Water Environment Testing and Evaluation Research Center of the Ministry of Water Resources.   All working standards were prepared using ultra-high purity water.

Apparatus

In this study, the GPMAS instrument (CGM800 automatic COD_{Mn} analyzer) that was designed, modified and applied to COD_{Mn} determination for water samples was provided by Shanghai Beiyu Analytical Instrument Co., Ltd.   The working scheme of this GPMAS-based COD_{Mn} analyzer is shown in Fig. 1, and the critical instrumental parameters are shown in Table 1.

Methods and principle

The method was based on oxidation of organic compounds by $KMnO_4$ and subsequent titration of excessive $NaNO_2$. Firstly, 100 mL of water sample was placed in the online digestion device.   The digestion device automatically added 10 mL of $KMnO_4$ standard solution (approximately equal to 0.01 mol/L) and 10 mL of 1 + 3 (V + V) H_2SO_4 solution into the sample bottle, and this was followed by digestion for 30 min in a near boiling water bath.   Then, the instrument automatically added 10 mL of $NaNO_2$ standard solution (0.01 mol/L) to completely reduce the potassium permanganate.   The residual $NaNO_2$ was rapidly converted to NO_2 in HCl/ethanol solution.   Then the NO_2 was carried by N_2 into the GPMAS at a flow rate of 9 mL/min for detection.   For spectrometric detection, a deuterium
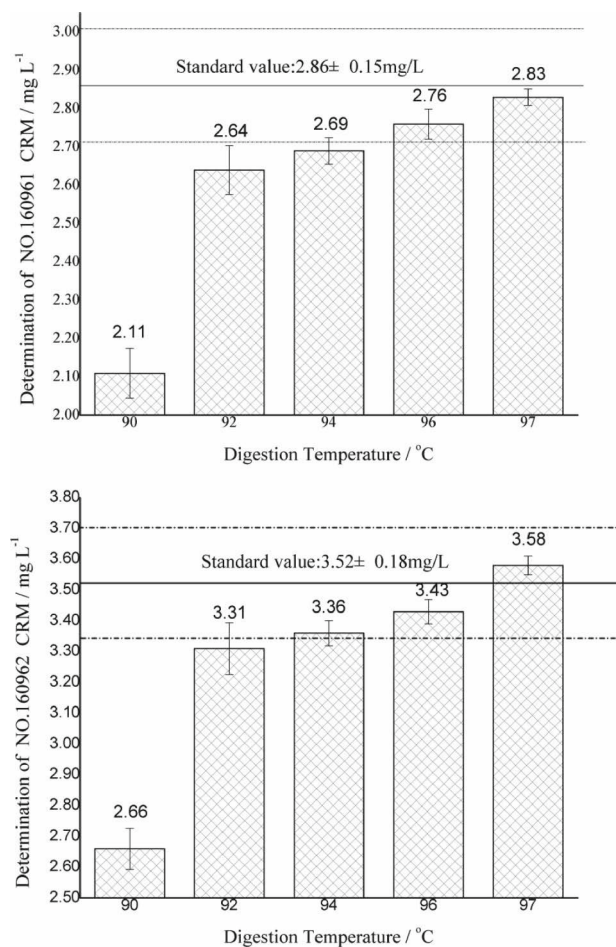
Fig. 2   Effect of digestion temperature on COD_{Mn} determination using developed GPMAS method. Digestion time: 30 min; ratio of sulfuric acid (V + V): 1 + 3.

lamp was used as a light source with a wavelength of 213.9 nm, and light path length was set at 24 cm in order to obtain satisfactory sensitivity and precision. Finally, the instrument performed a reverse regression calculation based on the measured peak heights, and obtained the permanganate index of the water sample. A delay time of 40 s was selected for sufficient time gap between cycles (Fig. 1).

Results and Discussion

Optimization of GPMAS method

Traditional COD_{Mn} standard methods, such as international standard ISO 8467-1993, Japanese standard JIS K0102, and Chinese standard GB 11892-89, are all empirical titration experiments under well-defined conditions. Due to the considerable differences between different standard methods, it is important to follow the specific procedure of the applied standard to ensure validity of the obtained results using the GPMAS method. In this study, selected critical parameters, namely digestion temperature, digestion time and sulfuric acid concentration, were optimized, and these results were further compared to certificated values of the applied CRMs.

Effect of digestion temperature

Digestion temperature is an important condition that determines the oxidization amount of reductive organic compounds in a water sample.[29] Most standard methods, such as Chinese standard GB 11892-89, require the digestion of the water samples in boiling water to allow for sufficient oxidization. However, "boiling water" is a relatively ambiguous concept since the boiling point of water changes with different altitudes as well as salt contents. Additionally, it is tedious and troublesome, if even possible, to keep a water bath boiling without causing water level or temperature fluctuations. It is of great practical importance to develop COD_{Mn} analysis methods that can accurately and constantly maintain digestion temperature with convenience.

In this study, the effect of digestion temperature on the performance of the developed GPMAS method was evaluated. The digestion process was performed in the water bath, where the temperature was monitored and controlled by the autosampler. During the experiment process, the water temperature was measured using a thermometer, and no obvious difference between the thermometer and autosampler was observed. Various digestion temperatures, namely 90, 92, 94, 96, and 97°C, were examined with 30 min digestion time. As shown in Fig. 2, two COD_{Mn} CRMs, including No. 160961 with a certificated value of 2.86 ± 0.15 mg/L and No. 160962 with a certificated value of 3.52 ± 0.18 mg/L, were analyzed. When the digestion temperature was 90°C, the obtained COD_{Mn} determination for both CRMs were much lower than other temperature values, indicating an inadequate oxidization ratio due to a relatively low reaction rate at insufficient temperatures. Gradual increases in COD_{Mn} determination for both CRMs were observed with an increase in digestion temperature. The most satisfactory results were obtained at the digestion temperature of 97°C, when the relative error was only 1.05% for No. 10961 and 1.70% for No. 160962, exhibiting superior accuracy of this developed method. Hence 97°C was chosen as the digestion temperature for further experiments.

Effect of digestion time

Digestion time is another critical parameter that directly influences the oxidization of substances in a water sample. The required digestion time varies in different standard methods. For example, the water sample should be digested for 30 min in JIS K0102, while ISO 8467-1993 only requires digestion time of 10 ± 2 min. The digestion time is set at 30 ± 2 min in GB 11892-89, and a longer digestion time results in a higher oxidization ratio. One should always follow the particular requirement of digestion time for applied the standard method in detail to ensure valid measurement.

In this study, the effect of digestion time was studied by digesting CRMs at 97°C from 10 to 50 min. The certificated values of two applied CRMs were 2.86 ± 0.15 mg/L for No. 160961, and 3.52 ± 0.18 mg/L for No. 160962, respectively. These results are shown in Fig. 3. It was noticed that the obtained COD_{Mn} determinations for both CRMs were significantly lower than certificated values as digested time was 10 min, which is due to insufficient oxidization of substances in water samples. The COD_{Mn} determinations increased continuously with increasing of digestion time, and the smallest relative errors were obtained between COD_{Mn} determinations and certificated values for both CRMs when digestion time reached 30 min. When length of digestion time further increased to 40 and 50 min, the obtained COD_{Mn} results continued to increase and exceeded the acceptance limits of certificated values. The digestion time of 30 min was selected as optimized the digestion time in order to achieve the best reliability.
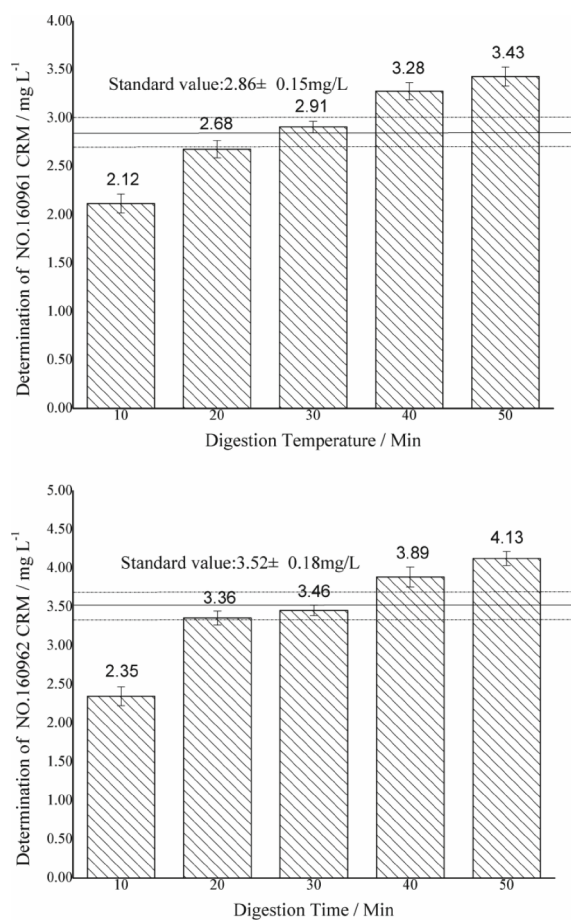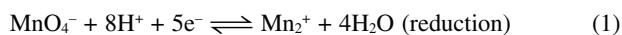
Fig. 3 Effect of digestion time on COD_{Mn} determination using developed GPMAS method. Digestion temperature: 97°C; ratio of sulfuric acid (V + V): 1 + 3.

Fig. 4 Effect of sulfuric acid content on COD_{Mn} determination using developed GPMAS method. Digestion temperature: 97°C; digestion time: 30 min.

Sulfuric acid content

The acidity of the water sample plays an important role in the oxidization process of COD_{Mn} measurement. The half-reaction of permanganate oxidizing sample at elevated temperature is as follows:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn_2^+ + 4H_2O \text{ (reduction)} \quad (1)$$

Theoretically, the oxidization efficiency should increase with high sulfuric acid content since increased H^+ concentration could push the equilibrium to move to product side. In this study, the effect of sulfuric acid content on the measured COD_{Mn} values was investigated by varying sulfuric acid/water volume ratio from 1 + 1 to 1 + 11 (V + V). The examined CRMs were No. 170543 with a concentration of 1.66 ± 0.12 mg/L and 170545 with a concentration of 3.73 ± 0.22 mg/L. As illustrated in Fig. 4, when the sulfuric acid contents were 1 + 1 and 1 + 2 (V + V), the two CRMs were undetectable using the developed method. This is due to the fact that NO_2^- and H^+ would form unstable HNO_2 in a highly acidic environment, which could decompose during the digestion process. When sulfuric acid content decreased to 1 + 3 (V + V), satisfactory results were obtained, generating a relative error of 1.20% for No. 170543 and 0.80% for No. 170545. The measured COD_{Mn} determination continued decreasing with a further decrease of sulfuric acid content and no longer remained within the acceptance limits of the two studied CRMs. This observation was in accordance
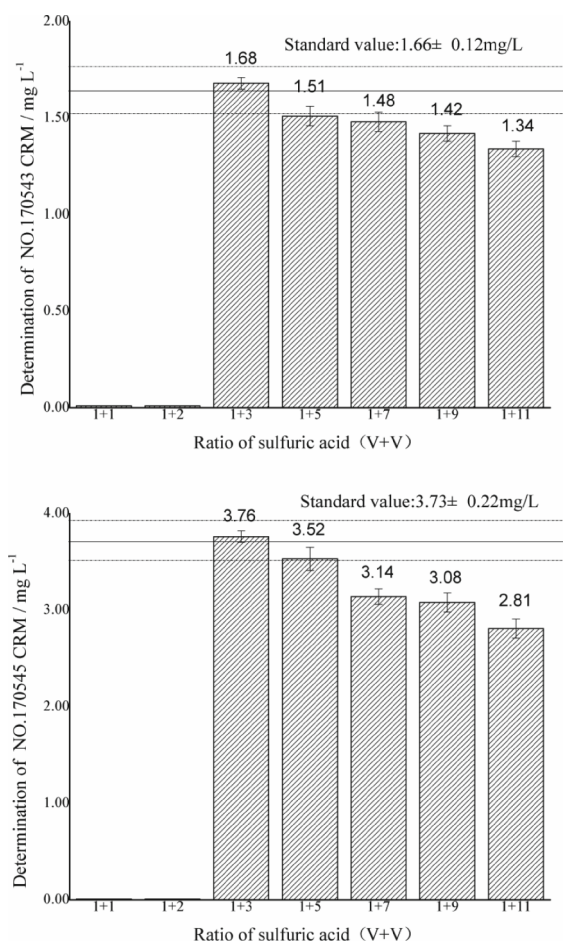
with the theoretical prediction that a lower H^+ concentration would cause Eq. (1) to move to the reactant side.

Evaluation of method performance

The developed GPMAS method was evaluated by characterizing the analytical performance in terms of calibration linearity, standard deviation of the regression, linear range, limit of detection (LOD), reproducibility and accuracy. The figures of merit of the calibration curves are listed in Table 2. For comparison purposes, a summary of characteristic performance data for several FIA-based COD_{Mn} and the ISO standard method are also included. Generally, the performance of this developed GPMAS method is comparable or superior to other methods. A calibration curve of COD_{Mn} standard was constructed by analyzing a series of sodium nitrite solutions with concentrations varying from 0.20 to 4.00 mg/L under the optimized experimental condition. The obtained linear range of the developed GPMAS method was 0.35 – 12.0 mg/L with the correlation coefficients (R) of 0.999. The LOD was calculated based on three times the standard deviation of the signal intensity obtained from 20 duplicated blank samples divided by the slope of the calibration curve. The LOD of the developed method was 0.12 mg/L, which is significantly lower than that of GB 11892-89 (0.5 mg/L) as well as that report in most of literature (Table 2), suggesting considerable improvement of sensitivity. The reproducibility of the method was determined by five repeated measurements

Table 2   Comparison of developed GPMAS method and existing methods

Method	Linear range/mg L^{-1}	Precision RSD, %	LOD/mg L^{-1}	Sampling rate/h^{-1}	Ref.
FIA	0 – 170	0.5	10	20	30
FIA with on-line oxidation	0.5 – 50	1.2 – 2.7	0.5	30	31
FIA with on-line regeneration of KMnO$_4$	1.0 – 24	0.4	0.5	30	32
FIA with chemiluminescence detection	0.2 – 20	2.1	0.08	8	33
Titrimetric methods	0.5 – 10	1.21 – 5.46	0.5	4	ISO standard method[a]
GPMAS	0.35 – 12.0	0.71 – 2.37	0.12	30	This work

a. <ISO 8467-1993 water quality-determination of permanganate index>, an ISO (International Organization for Standardization) standard COD$_{Mn}$ determination method that has been widely adopted for water quality monitoring.

Table 3   Determination of CRMs using developed GPMAS method

Sample	Certificated value/ mg L^{-1}	Determination[a]/ mg L^{-1}	Relative error, %
106960	2.02 ± 0.11	1.99 ± 0.03	1.5
106961	2.86 ± 0.15	2.91 ± 0.03	1.7
160962	3.52 ± 0.18	3.44 ± 0.03	2.3
161341	3.80 ± 0.34	3.75 ± 0.08	1.3
203164	4.67 ± 0.46	4.55 ± 0.11	2.6
203165	1.54 ± 0.16	1.44 ± 0.02	6.5
203166	3.42 ± 0.27	3.54 ± 0.03	3.5

a. Standard deviation was determined after performing five (5) measurements.

Table 4   Application of developed GPMAS method to real water samples and comparison with conventional titrimetric method (GB 11892-89)

Water sample	GPMAS method[a]/ mg L^{-1}	Titrimetric method[a]/ mg L^{-1}
CRM 160962[b]	3.44 ± 0.03	3.50 ± 0.04
Yangtse River	2.03 ± 0.02	2.05 ± 0.04
Dongting Lake	2.74 ± 0.03	2.77 ± 0.05

a. Standard deviation was determined after performing five (5) measurements.
b. Certificated value: 3.52 ± 0.18 mg/L.

Table 5   Recoveries in COD$_{Mn}$ determinations with spike test

Water sample	Initial/ mg L^{-1}	Added/ mg L^{-1}	Found/ mg L^{-1}	Recovery, %
203164	4.55[a]	3.00	7.54	99.7
203165	1.44[a]	3.00	4.51	102.3
Yangtse River	2.03	3.00	5.12	103.0
Dongting Lake	2.74	3.00	5.68	98.0

a. Initial COD$_{Mn}$ values were determined using developed GPMAS method.

using seven different CRMs. The obtained relative standard deviation (RSD) ranged from 0.71 to 2.37% at various concentration levels. The analytical frequency was 30 samples per hour, revealing the potential of the developed GPMAS method as a high-throughput analytical technique for routine water quality monitoring. In order to evaluate the accuracy of the developed method, seven different CRMs were analyzed. As shown in Table 3, the COD$_{Mn}$ determinations obtained by the developed GPMAS method were all in good agreement with the certificated values.

Application to real water samples
The developed GPMAS method was applied to the analysis of real water samples collected from the Yangtse River and Dongting Lake, and the results were compared to that obtained using the GB 11892-89 standard method. CRM No. 160962 with a certificated concentration of 3.52 ± 0.18 mg/L was also included in this comparison. As demonstrated in Table 4, the results obtained by using the GPMAS method and traditional titrimetric method were almost identical to each other, demonstrating the accuracy and reliability of the developed GPMAS method. Matrix effects were investigated by spiking COD$_{Mn}$ standards in both real water samples as well as two CRMs. As shown in Table 5, the recoveries in COD$_{Mn}$ values from different CRM and real water samples varied from 98.0 to 103.0%. The results reveal that matrix complexity had little effect on the recovery using the developed GPMAS method.

Conclusions

Accordingly, a quick GPMAS method was developed to determine COD$_{Mn}$ in water samples for the first time, using gas-phase molecular absorption spectrometry equipped with an on-line automated digestion device. Satisfactory results can be obtained with a sulfuric acid solution ratio of 1 + 3 (V + V),

digestion temperature of 97°C, and digestion time between 20 to 30 min. This developed method exhibited good linearity in the range from 0.35 to 12 mg/L (r = 0.9999), a detection limit of 0.12 mg/L, and RSD of 0.71 – 2.37%. Spiked recovery results of different samples were found between 98.0 and 103%. The developed method demonstrated no significant difference from the traditional titration method when used to analyze the standard solution and real water samples. Moreover, this method was fully automated, simple and rapid, and not influenced by environmental temperature fluctuations and human error. Due to the significantly improved speed, stability and accuracy, the developed GPMAS method can be adopted as an ideal alternative to the traditional titrimetric method for COD$_{Mn}$ determination in routine water quality monitoring.

Acknowledgements

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