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# Research of a portable rapid in situ monitoring system for the determination of COD in waters

WEI KANG-LIN[a,b,c], WEN ZHI-YU[a,b,c], HUANG ZHENG-YONG[d], MO ZHI-HONG[d]
[a]*National Center for International Research of Micro/Nano-Systems and New Material Technologies, China*
[b]*National Key Disciplines Laboratory of New Micro/Nano Devices and Systems, China*
[c]*Microsystem Research Center, Chongqing University, Chongqing, 400044, China*
[d]*College of Chemistry and Chemical Engineering of Chongqing University, Chongqing, China*

A portable rapid monitoring system for in situ measuring chemical oxygen demand (COD) of environmental water samples is described. Integrating with the on line sample chemical pretreatment of ultrasound-assisted Fenton reagents digestion of organic compound at normal temperature and normal pressure, system adopts the method of competition for hydroxyl radical between organic compounds and the chromogenic reagent for determination of COD content in water samples. The microspectrometer with the function of continuous spectrum analysis is the core of the system, and the multifunction miniature sample reacting and detecting chamber is the key technology. The system prototype machine can in situ measure the COD content in water samples, and it has a throughput of 3 measurements per hour, a LOD (limit of detection ) of 3.5mg/L, a linear response over the calibration range of 0-30mg/L ($R^2$ = 0.9976), and a precision of 4.3% RSD at 15mg/L (n = 7). Field evaluation of the system prototype machine and detection method had been performed in Chongqing water environment monitoring center and a sewage treatment plant in Chongqing city, where a lot of different environment water samples had been measured over two months by contrast with China’s national standard lab analysis method for determination of COD. Good agreement was observed between the samples’ determination data from China’s national standard lab analysis method and those in situ measured by the system prototype machine. Moreover, the system prototype machine has quite a few technical advantages, such as small volume, low cost, lower power and much shorter measuring time (1/6 of the average). Therefore, it meets the practical demands of modern water quality monitoring and forecasting net.

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*Keywords:* COD, Microspectrometer, Digestion, In situ water quality measuring

## 1. Introduction

COD is a comprehensive water quality index which is commonly used to show the degree of organic pollution for water, and it is also an important water quality parameter which must be measured for water pollution monitoring and controlling. So it is necessary for the research and development of in situ monitoring instrument for COD.

The standard evaluation procedure of water quality is water sampling followed by sample storage, transport, handling and then analysis in lab, and this method is cost-intensive and not able to provide large data sets of spatial distributions or temporal trends of such water quality parameter as COD. Moreover, the probability of sample degradation during off-site filtration, transport and storage may mislead to the wrong evaluation for water quality [1]. So the in situ measurement avoids many of these complications, and if rapid automated instruments are used for this purpose, there is the potential of obtaining intensive spatial and temporal data for COD in water [1].

So far there are several detecting principles which had been developed for on-line monitoring COD, such as dichromate-titration, dichromate-spectrophotometry, UV absorption spectrum analysis and hydroxyl radical oxidation –electrochemical analysis [2]. Among these detection methods, the dichromate method is considered as the main one utilized for instrument development, but it has such shortcomings as the need of extremely complicated instrument structure for the digestion of water samples at high temperature and pressure, long time for the determination of COD, reagents with high cost and serious secondary pollution, which make it difficult for the contemporary “green” analysis. Although the method of UV absorption spectrum analysis for determination of COD doesn’t need reagents, the poor linear correlation between the absorbance and COD concentration may cause the intelligent algorithm model affected by the different water body, and so this method has poor stability and universality [3-5]. Compared with the three methods above, the method of hydroxyl radical oxidation – electrochemistry analysis without any secondary pollution can satisfy the need of the fast determination of COD in water at normal pressure and temperature, but the lifetime of the sensor electrode will be shortened by various pollutants when contacting with the water.

In order to satisfy the demands of modern water quality monitoring technology and networks, an ideal in situ monitoring system should have the following characteristics: light-weight, low power consumption, economic use of stable reagents, reliability and durability, simplicity and low cost[6-8]. And analytical features such as accuracy, high sample throughput, sensitivity and precision are also required to scientifically evaluate water quality.

In the presented work a rapid in situ monitoring system for the determination of COD in waters based on MOEMS (micro-optical electronic mechanical system) microspectrometer's continuous spectrum analysis and efficient sample chemical pretreatment has been reported, and the results of the system's application for on line determination of COD in natural waters and waste waters have shown that system meets the demands of modern water quality monitoring technology and networks.

## 2. Design of the monitoring system

### 2.1 Efficient sample chemical pretreatment

### *2.1.1 Pretreatment and spectrum detection*

The mechanism of sample chemical pretreatment is the competition for hydroxyl radical between organic compounds and the chromogenic reagent.

The $Fe^{2+}$ as a catalyst in acid medium is able to accelerate the $H_2O_2$ decompose to produce hydroxyl radicals (·OH) with strong oxidizing ability [9-10], which can cause the beginning of hydroxyl radicals' chain reaction at the same time (Fig. 1). The whole reacting system is very complicated, and the arousal and transfer function of $Fe^{2+}$ takes an important role, which makes the chain reaction continue until $H_2O_2$ is exhausted [11]. The essence of Fenton reagents ($Fe^{2+}$ and $H_2O_2$) digesting organic compounds is that organic compounds is oxidized to the water and carbon dioxide because hydroxyl radicals' strong oxidizing ability can make organic compounds' H (atoms) taken off and C-C keys ruptured.

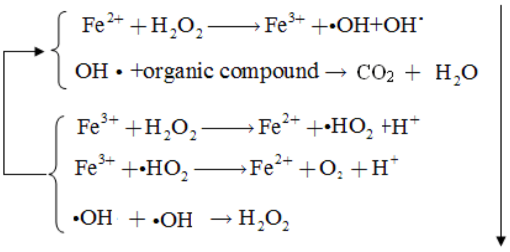

*Fig. 1. Mechanism of sample's chemical pretreatment.*

Both the organic compounds and the chromogenic reagent can be oxidized to the water and carbon dioxide by the hydroxyl radical (·OH). But under the condition that the hydroxyl radical's oxidizing ability for organic compounds is stronger than for the chromogenic reagent [12-13], the remaining hydroxyl radicals will continue to react with chromogenic reagent once the common organic compounds in the water sample had been digested completely. So, if the COD content in the water is high, there will be less remaining hydroxyl radicals, then there will be less chromogenic reagent to be digested, which lead to the absorbance of the remaining chromogenic reagent to be high, that is to say, there is a linear relationship between the COD content and the absorbance of the remaining chromogenic reagent. Therefore, the COD content of the water sample will be determinated by measuring the remaining chromogenic reagent's spectrum at its characteristic absorption wavelength of 610 nm.

This determination method for COD has such technical advantages as fast digestion, small amount of reagents and no secondary pollution, which can make the design of monitoring instrument satisfied for the technical demands of rapid in situ measuring and "green" analysis [14-15].

### *2.1.2 Ultrasound-assisted digestion*

Ultrasound-assisted digestion can be used to speed up the sample's digestion reaction [16-17]. When ultrasound acts on the sample reaction system of certain volume, ultrasound cavitation can produce micro jet with strong impact force, instantaneous high pressure and high temperature,with the function of fragmentation, agitation, tepefaction, and emulsification to organic compounds in the water sample.And the results of lots of experimental researches have showed that ultrasound-assisted digestion can accelerate sample chemical pretreatment reaction and improve the efficiency of digestion for common organic compounds in water.

### 2.2 Design principles and key technologies of the monitoring system

### *2.2.1 Design principles*

In order to reduce the volume ,cost and power of the monitoring system , the MOEMS based microspectrometer (Fig. 2) self-developed by our research center was used as spectrum detection device. And because spectrum signal processing algorithm can play an important role in the range of microspectrometer's continuous spectrum (340-800 nm), the spectral measurement precision of determination for orthophosphate should be greatly improved.

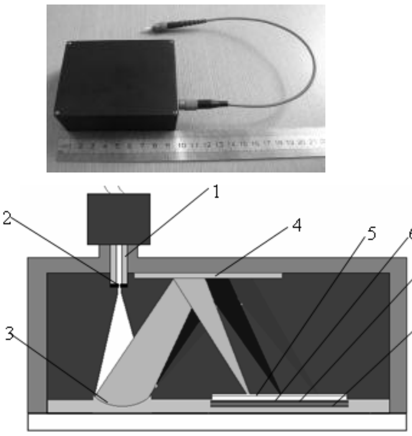

*Fig. 2. MOEMS based microspectrometer with opticalfiber(1), slit(2), holographic concave grating(3), plane mirror(4), cylindrical lens (5), light filter (6), color filter(7),CCD(8).*

According to Lambert-Beer law, the small monitoring system prototype machine (Fig. 3) for in situ measuring COD based on ultrasound-assisted Fenton reagent digestion and microspectrometer's continuous spectrum analysis had been designed, and system is mainly composed of flow paths system, miniaturized spectral analytical system and embedded measuring & controlling system.

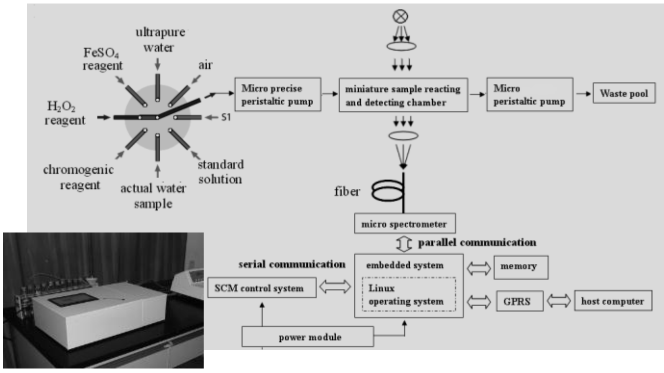

*Fig. 3. The Monitoring system for in situ measuring COD.*

While system running, the water sample and chemical reagents are sequentially injected to the sample reacting and detecting chamber according to a precise volume ratio by the flow paths system based on micro precise peristaltic pump and multi-position valve. The on-line pretreatment, including digestion reaction and chromogenic reaction, takes place in the miniature sample reacting and detecting chamber, after spectrum detection for the sample reaction system, system sends the measuring data to host computer by GPRS. After measurement of one copy of water sample, the system self-cleans the sample reacting and detecting chamber, and then continues to measure the COD content in the next copy of water sample.

### *2.2.2 Key technology*

The MOEMS based microspectrometer is the core of the spectrum detection system, but the miniature sample reacting and detecting chamber with multifunction is a key technology of the monitoring system. Because the on-line chemical pretreatment demands that system must have the controlling functions of self-stirring, self-cleaning and constant temperature, based on the ultrasonic technology and the principle of constant temperature water bath, a miniature sample reacting and detecting chamber with the functions of spectrum detection, ultrasonic agitation, ultrasonic cleaning, and constant temperature had been designed on the condition that there is no effect on optical path for spectrum detection.

Moreover, the ultrasound-assisted digestion can also accelerate the chemical pretreatment for digesting COD in the water sample. The structure of the sample reacting and detecting chamber is shown in Fig. 3, and all of the above controlling functions can be realized by SCM (single chip microcomputer) control system.

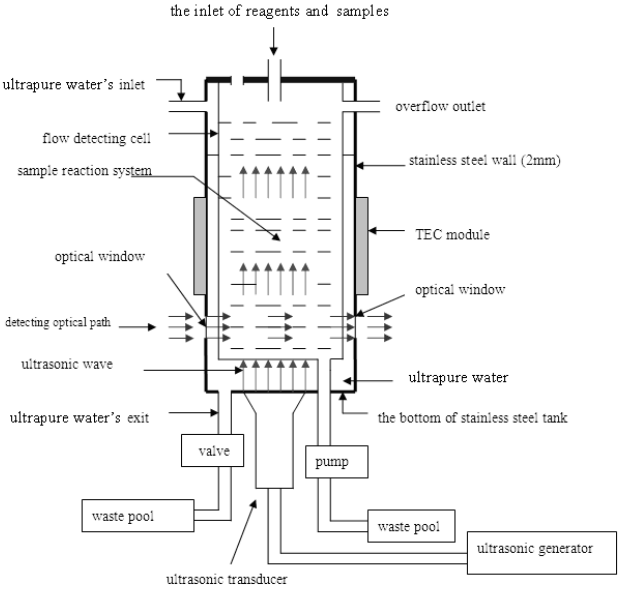

*Fig. 4. The multifunction reacting and detecting chamber.*

### *2.2.3 System 's working process*

While monitoring, the host computer sends out the instruction of responding after power up, and then the monitoring system starts to self-check. After self-checking, it begins to measure COD content in the water sample, and the measuring data can be sent to the host computer by GPRS. Fig. 5 shows the system's working process for on-line determination of COD in the water samples.

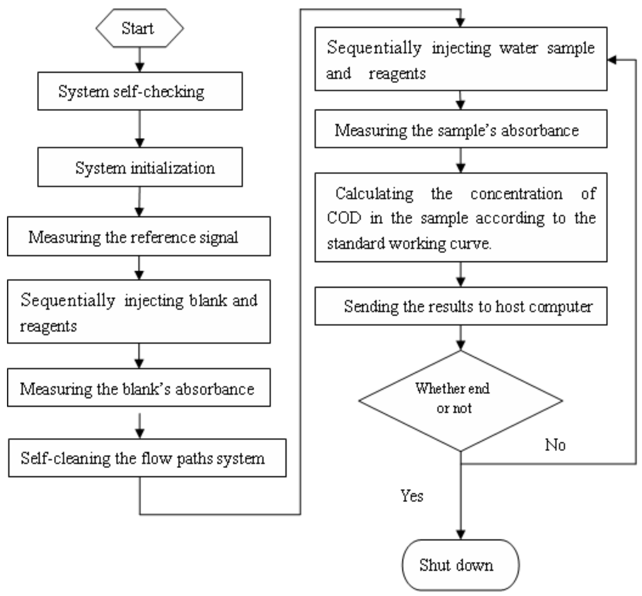

*Fig. 5. Monitoring system's working process.*

## 3. Results and discussion

### 3.1 Three-wavelength spectral analysis method

Aiming at the determination of COD in the actual water sample, our experiment research has proved that the background interference of the actual water sample can be effectively eliminated by multi-wavelength spectral analysis method (see eq. (1)). So the multi-wavelength spectral analysis can be applied in our monitoring instrument for COD because of the microspectrometer's continuous spectrum measurement, and the precision and accuracy for on-line measuring COD had been greatly increased [18-19].

$$\Delta A = A_{610} - 0.35A_{480} - 0.65A_{680} \qquad (1)$$

Further experiment researches had proved the correctness of the above measurement conditions and the multi-wavelength spectral analysis method for COD, as can be seen from Fig. 6 and Fig. 7. Fig. 6 shows the spectra of different COD standard solutions in a wavelength region between 450 and 700 nm, and the dependency of the COD's concentration on the absorbance based on is demonstrated in Fig. 7. Such dependency called as standard working curve is the measuring basis for COD.

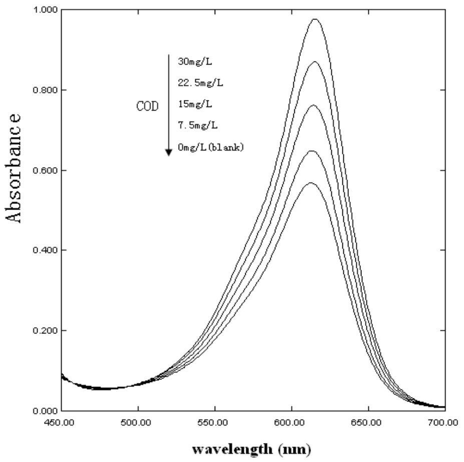

*Fig. 6. The absorbance curve of COD in deionised water.*

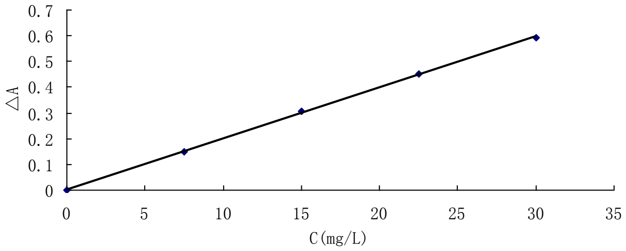

*Fig. 7. Correlation between absorbance and COD concentration.*

### 3.2 Measurement of the standard samples of COD

Precision and accuracy are two important parameters which are characterization of instrument's stability. After the equation of calibration curve being established, the instrument's stability had been tested for three months by measuring China's national standard sample of COD. Table 1 shows one random test result. In the case of the given concentration, a strong correlation between the standard sample's concentration and the measured data from the instrument occurs. and the results show that the monitoring system prototype machine has high accuracy (relative error ≤5%).

*Table 1. Results of the instrument's application on given standard sample of COD.*

| Given concentration (mg/L) | Instrument's measuring value (mg/L) | Relative error (%) |
|---|---|---|
| 15.0 | 14.7 | -2 |
| 20.0 | 19.3 | -3.5 |
| 30.0 | 28.8 | -4 |
| 24.0 | 24.7 | 2.9 |
| 18.0 | 18.8 | 4.4 |
| 7.0 | 6.7 | -4.3 |
| 10.0 | 10.3 | 3 |

Moreover, the monitoring system prototype machine has a high precision (repeatability) too. The standard COD sample with the concentration of 15mg/L being used as test sample, seven copies of the same water sample had been continuously measured, and the results shows that the system prototype machine has a precision of 4.3% RSD at 15mg/L (n = 7).

In conclusion, the Measurement of the COD standard samples proves that the monitoring system prototype machine has strong stability.

## 3.3 Application experiment

### 3.3.1 Digestion and measurement conditions

Because the COD content is higher in lakes, aiming at the same water sample collected from a local lake(Fig.8) and taking the measured data by China's national standard lab analysis method for determination of COD as an evaluation criterion, we had investigated the sample digestion ratio's variation with the time of ultrasound-assisted digestion (Fig. 9). And it can be seen from Fig. 8 hat the sample digestion ratio can reach to 99.7% on the condition that ultrasound-assisted digests for 19min and at the normal pressure the temperature is controlled at 30℃.

*Fig. 8. The source of the measured water samples.*

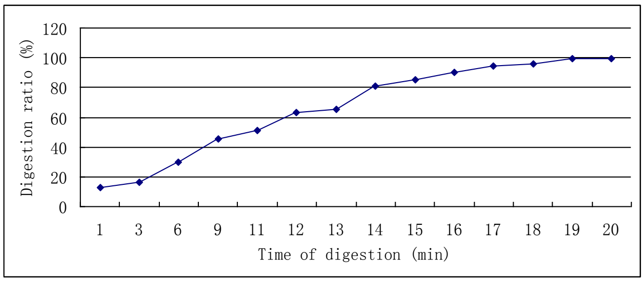

*Fig. 9. The digestion ratio's variation with the time of ultrasound assisted digestion.*

### 3.1.2. Monitoring COD in the sewage treatment plant's discharged wastewater

In order to verify the reliability and feasibility of the instrument monitoring COD in the actual water sample, the measured data by China's national standard analysis method for COD were taken as a evaluation criteria, and the spot experiment had been carried out to contrast instrument with China's national standard analysis method for measuring COD in the discharged water of a the sewage treatment plant in Chongqing city (Fig. 10). And Fig. 11 shows the detecting spectrum of the discharged water.

(a) Discharged water of the sewage treatment plant

(b) The field contrast experiment

*Fig. 10. Contrast experiment between instrument and China's national standard analysis method.*

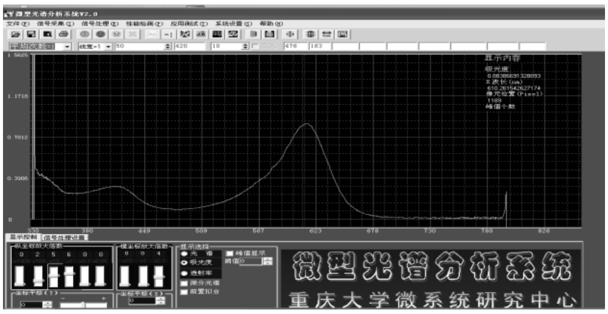

*Fig. 11. The detecting spectrum of COD in wastewater.*

The contrast experiment had been carrying out for 7 days, and Table 2 shows the results of the experiment.

*Table 2. The results of the contrast experimentbetween our monitoring instrument and China's national standard analysis method for measuring COD in the waste water.*

| Date of test | COD conctent (mg/L) (from Chian's national standard anlysis method) | COD conctent (mg/L) (from our monitoring instrument) | Relative error (%) |
|---|---|---|---|
| 3 August 2011 | 22.3 | 21.8 | -2.2 |
| 4 August 2011 | 24.9 | 25.3 | 1.6 |
| 5 August 2011 | 23.8 | 22.9 | -3.8 |
| 6 August 2011 | 24.1 | 24.8 | 2.9 |
| 7 August 2011 | 25.9 | 26.3 | 1.5 |
| 8 August 2011 | 24.4 | 23.7 | -2.9 |
| 9 August 2011 | 24.8 | 23.8 | -4.0 |

Mathematical statistics analysis for the two teams of measured data in Table 2 shows that there aren't notable differences between the instrument's measured data and those by China's national standard analysis method for determination of COD. Therefore the consistency of the data between the instrument's measured data and the measured data from China's national standard analysis method for COD is very strong, and the instrument can meet the demands of on-line determination COD in the actual water sample.

## 4. Instrument's technical parameters & technical advantages

The application of the monitoring instrument have proved that it can meet the technical specifications of China's environmental protection standard, and Table 3 shows the key technical parameters of the instrument.

*Table 3. Instrument's key technical parameters.*

| Technical parameters | |
|---|---|
| Linear range(mg/L) | 0.05-45 (can be adjusted) |
| LOD(mg/L) | 0.05 |
| Accuracy | ±5% |
| Precision | 5% |
| Measuring time | 20 min |
| Volume | 500 mm×310 mm×165 mm |
| Power | 48W |
| Weight | 9.8kg |

Moreover, the automatic monitoring instrument has quite a few technical advantages, such as small volume, low cost and much shorter measuring time (1/6 of the average) and products without secondary pollution. Therefor, the instrument meets the demands of modern water quality monitoring and forecasting net.

## 5. Conclusion

The rapid monitoring instrument for COD in water based on efficient sample chemical pretreatment and microspectrometer's continuous spectrum analysis had been developed. And the comparative experiment with China's national standard analysis method for measuring COD had demonstrated that the key technical indexes of the instrument such as the precision and the accuracy are superior to the technical requirement of environmental protection product in China. Moreover it has such technical advantages as small volume, multifunction, low cost, much shorter measuring time (1/6 of the average) and products without secondary pollution. Therefore, the instrument meets the demands of on-line determination of the COD for actual water sample.

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[*] Corresponding author: zeyuanwei@163.com