

# Rapid Determination of Chemical Oxygen Demand by Flame AAS Based on Flow Injection On-line Ultrasound-assisted Digestion and Manganese Speciation Separation

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## INTRODUCTION

Chemical oxygen demand (COD) refers to the amount of oxygen necessary for the oxidation of all organic matter contained in a water sample; it is a widely used parameter in controlling the degree of pollution in water and managing effluent quality. The conventional and standard method for COD determination consists of two steps: (a) oxidizing digestion by adding a strong oxidant such as potassium permanganate or potassium dichromate to the given samples of water and refluxing at high temperature, and (b) titration of excess oxidant (1,2). This methodology is manual and suffers from a series of drawbacks such as being very time-consuming (two hours are required for digestion plus time for titration) and requiring a high amount of expensive ( $\text{Ag}_2\text{SO}_4$ ) and toxic ( $\text{HgSO}_4$ ) chemicals. Much effort has been devoted to the improvement and alteration of the standard manual method, and many research results have been reported (3–20).

Flow injection analysis (FIA) is becoming one of the most important tools for routine work because it is a simple and inexpensive method with high analysis speed, high precision, and suitable for on-line analysis. These advantages make FIA especially interesting for routine COD determinations. Korenaga and co-workers made the first attempts in this respect and reported the possibility of determining COD using the FIA techniques with potassium perman-

## ABSTRACT

A rapid flame atomic absorption spectrometry (FAAS) method for the determination of chemical oxygen demand (COD) is proposed. It is based on using ultrasonic wave to advance sample digestion by potassium permanganate and flow injection on-line speciation separation of manganese. In a digestion coil, placed in the ultrasonic and heating water bath, the sample was oxidized by acidic potassium permanganate to produce  $\text{Mn}^{2+}$ . Passing through a cooling coil,  $\text{Mn}^{2+}$  was adsorbed on a cation-exchange micro-column, while the unreduced  $\text{MnO}_4^-$  passed through the micro-column to waste. Then the adsorbed  $\text{Mn}^{2+}$  was eluted reversely by  $3 \text{ mol L}^{-1}$  HCl and determined by FAAS. With a digestion temperature of  $80^\circ\text{C}$  and a digestion time of 30 s, the determination range was  $3\text{--}300 \text{ mg L}^{-1}$  COD and the detection limit was  $1 \text{ mg L}^{-1}$  COD, with a sampling frequency of 24 samples per hour. The relative standard deviation of the method was 2.7% ( $n=9$ ). Chloride did not interfere up to the  $1000\text{-mg L}^{-1}$  level. The proposed method was applied to the determination of COD in well, river, and pool water samples, and the results obtained are in agreement with those given by the standard methods.

ganate (3,4), potassium dichromate (5), and with Ce(IV) (6) as the oxidant. Further studies were done by Appleton (7), Balconi (8), and Pecharroman (9). Segmented flow analysis (SFA) to COD determination was applied by Tian (10).

All of the above-mentioned flow systems show higher analysis speed than the conventional method. However, the big difference in time required for heating digestions between the conventional method (2 h) and flow methods (a few minutes) means that in some cases there is a difference in the degrees of sample oxidation, with the possibility of a difference in COD values obtained. In order to enhance the efficiency of digestion, microwave radiation (MW) has been applied to the digestion step in a FIA system for COD determination (11–14). It is well known that ultrasonic waves can quicken chemical reaction and enhance productivity (21). In recent years, ultrasonic waves have been widely used in the destruction of organic pollutants (22,23) and oxidation digestion (24). Aiguo Zhong (15) recently presented a method for COD determination based on the use of ultrasonic digestion, but not with a FIA system.

Spectrophotometry is the most common detector used for COD determination by FIA, but this non-specific detector has some drawbacks. Signals are frequently unstable due to bubble formation, which imposes an upper limit to the applied temperature in the digestion step and causes a decrease in the degree of complete oxidation of the organic matter in the water sample. Flame atomic absorption spectrometry (FAAS) is superior in terms of speed, sensitivity, and selectivity, and is very suitable for metal determination in liquid samples. However, its application to COD determination is

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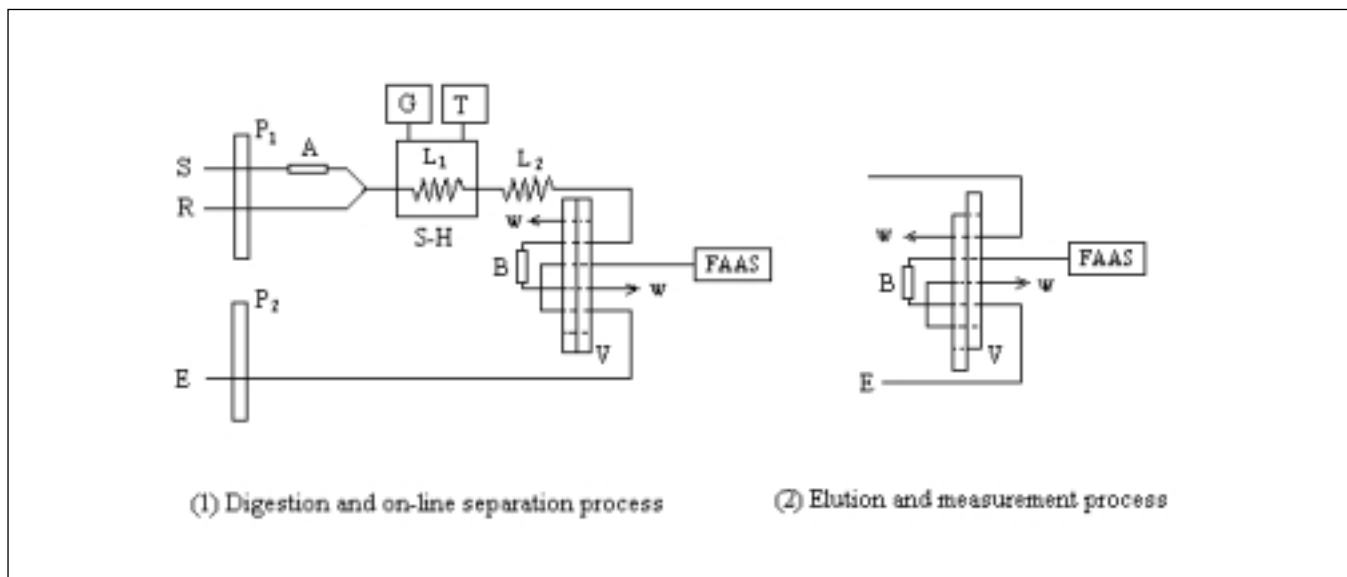


Fig. 1. Schematic of the ultrasound-assisted digestion/flow injection on-line separation system for the determination of COD. S = sample; R = acidic  $\text{KMnO}_4$  solution; E = water or HCl solution;  $P_1$  and  $P_2$  = peristaltic pumps;  $L_1$  = digestion reaction coil (about 1 mm i.d. and 500 cm in length, made of glass);  $L_2$  = cooling coils (1 mm i.d. and 50 cm in length); S-H = ultrasonic and heating water bath; G = ultrasonic generator; T = thermostat; V = injection valve; A and B = cation exchange micro-columns (2 mm i.d. and 50 mm in length); FAAS = flame atomic absorption spectrometer; W = waste.

hampered by the need of a separation step for different species of the same element such as Cr(VI) and Cr(III), Mn(VII) and  $\text{Mn}^{2+}$ . Cuesta et al. (13) presented a FI-FAAS for COD determination in which MW heating digestion of the sample with potassium dichromate was followed by ion exchange (13) or extraction (14), and separation of Cr(VI) from Cr(III). Recently, Lee et al. (16) proposed an electrochemical COD sensor and Kim et al. (17,18) proposed a photocatalytic sensor based on using an oxygen electrode for COD determination.

In this paper, a rapid ultrasonic digestion with a cation exchange column on-line separation of  $\text{Mn}^{2+}$  from Mn(VII) is proposed using a FI-FAAS system for COD determination. Satisfactory results were obtained in the determination of COD in well, pool, and river water samples.

## EXPERIMENTAL

### Instrumentation

A Model TAS-986 atomic absorption spectrometer (Beijing Purkinje General Instrument Corporation, P.R. China), equipped with a hollow cathode manganese lamp, was used to measure the absorbance of  $\text{Mn}^{2+}$ . The wavelength and lamp current used were 279.5 nm and 2.0 mA, respectively. About 1700  $\text{mL min}^{-1}$  of acetylene and 8000  $\text{mL min}^{-1}$  of air flow were employed to obtain a steady flame. A computer was used to record the absorbance peaks.

A Model IFIS-C intellectual flow injector (Xi'an Ruike Electron Equipment Corporation, P.R. China) was used to design the FI system.

A Model ACQ-600 ultrasonic generator (Shaanxi Xiangda Ultrasonic Technology Engineering Department, P.R. China) and a Model 501 thermostat (Shanghai Experimental Apparatus Factory,

P.R. China) were employed to provide ultrasound-assisted and heating digestion conditions.

### Design of Flow Injection System

The flow injection system used in this work was similar to the one used for the indirect determination of ciprofloxacin (25), but the reaction coil ( $L_1$ ) was placed in an ultrasonic and heating water bath. The use of  $\text{NH}_4\text{F}$  was replaced with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  to neutralize the acid in the digestion reaction mixture. The experimental results showed that the oxidation digestion in an ultrasonic-assisted system can be run in a lower acidic solution and neutralization with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  is not required. Thus the system is simplified as seen in Figure 1.

### Reagents and Standard Solutions

All reagents were of analytical-reagent grade and double distilled water was used throughout.

A solution of glucose was used as the COD standard solution.

Stock solution of glucose (COD=500 mg L<sup>-1</sup>) was prepared by dissolving 0.5160 g glucose in water, diluting to 1000-mL volume, then storing in a refrigerator.

Working solutions were prepared fresh daily by appropriately diluting the stock solution.

Potassium permanganate solution (2×10<sup>-3</sup> mol L<sup>-1</sup>) was prepared by dissolving 0.3161 g KMnO<sub>4</sub> in a 1000-mL brown volumetric flask and diluting to 1000-mL volume.

Hydrochloric acid solution was 3.0 mol L<sup>-1</sup>.

Amberlite IRC-120 resin (Xi'an Electric Power Resin Plant, particle diameter 0.3–1.2 mm) was purified in a conventional way (25), then soaked in 10% hydrochloric acid solution for 24 h. After washing with water, the resin was filled into a micro-column.

### Procedure

An analytical procedure consists of three processes: (a) digestion and on-line separation, (b) washing, and (c) elution and measurement.

When the injection valve is in the sampling position, the stream of the sample solution (S) first passes through a cation exchange micro-column (A) to remove the interferences of the cation ions, then merges with a stream of acidic KMnO<sub>4</sub> solution (R). The sample is oxidized, and MnO<sub>4</sub><sup>-</sup> is reduced in the digestion reaction coil (L1) using ultrasound and heating. Passing through the cooling coil (L2), the Mn<sup>2+</sup> produced by the reduction of MnO<sub>4</sub><sup>-</sup> is adsorbed on-line on another cation exchange micro-column (B), which is connected to the injection valve by PTFE tubes as a sample loop, while anion MnO<sub>4</sub><sup>-</sup> unreduced passes through micro-column (B) to waste. This is the digestion and on-line separation process (30 s).

When the valve is in the injection position, the first process consists of washing micro-column (B) for 30 s with water, then the Mn<sup>2+</sup> is adsorbed on micro-column (B) is eluted by the HCl solution to the nebulizer, and measured by FAAS.

## RESULTS AND DISCUSSIONS

### Optimization of Solution pH for Mn<sup>2+</sup> Adsorption

The solution pH value ranging from pH 1–7 was studied on the FI on-line adsorption of 0.5 mg L<sup>-1</sup> Mn<sup>2+</sup> on micro-column (B). The results showed that the optimum solution pH value for the adsorbing Mn<sup>2+</sup> on micro-column (B) was between pH 2–3. It was found that a lower or higher pH was not beneficial to adsorption.

### Digestion Condition Optimization

Digestion acidity, temperature, ultrasonic power, digestion coil, and concentration of potassium permanganate were taken as variables for the optimization of the digestion condition.

The effect of acidity on sample digestion with ultrasound (26.5KHz, 600W) and without ultrasound was investigated by adding different concentrations of H<sub>2</sub>SO<sub>4</sub> to the potassium permanganate solution for the determination of 100 mg L<sup>-1</sup> of COD, respectively. The results are shown in Figure 2. From these results, the following conclusions can be drawn: (a) the ultrasonic wave can advance the sample digestion at an acidity lower than 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; (b) the optimum acidity of ultrasound-assisted digestion is far lower than without ultrasound, the former being 0.1 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub> and latter being 1.0 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub>; (c) ultrasonic digestion is more suitable to the determination of COD in a FIA system, because a lower acidity can lessen the corrosion of the system. Therefore, a potassium permanganate solution containing 0.1 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub> was used in this study. This acid concentration is far lower than required in all previous reports.

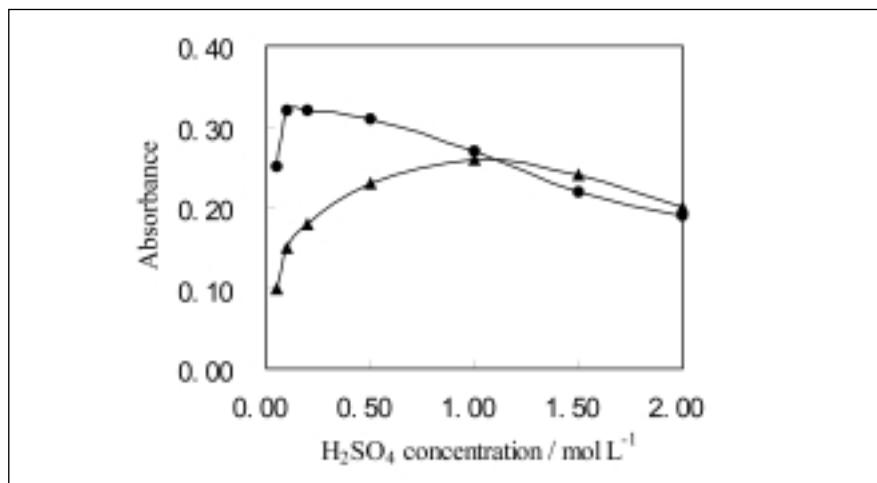


Fig. 2. The effect of acidity on sample digestion.  
 ●—●, with ultrasound-assisted digestion (26.5 kHz, 600W);  
 ▲—▲, without ultrasound-assisted digestion.

Temperature is an essential factor for most oxidation reactions. The influence of temperature on digestion was studied ranging from 20–90°C. The results show that the degree of digestion increased with a temperature up to 80°C; while above that temperature no significant increase was observed. The optimum digestion temperature for the ultrasonic wave and the heating water bath was set at 80°C.

The influence of ultrasonic power was investigated by adjusting the output power of the ultrasonic generator from 100–600 W at a fixed frequency of 26.5 KHz. As shown in Figure 3, the influence is slightly lower up to 200 W; then the digestion increases swiftly along with the measured absorbance with an increase in power from 200 to 500 W. Over 500 W, the influence remains virtually constant which most likely means that the digestion is complete. An ultrasonic power of 500 W was selected for this study. Using the acidity of 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, the digestion efficiency was tested once with ultrasound and once without ultrasound.

It was found that the ultrasonic wave declines quickly in plastics or rubber pipes (26). In order to avoid this absorbance, a glass pipe was chosen as the digestion reaction coil. At the time of the experiment, the glass digestion reaction coil was put into the ultrasonic and heating water bath. With an increase in the length of the digestion reaction coil (L1), the digestion time increases and the digestion reaction is more complete. With sample and acidic KMnO<sub>4</sub> solution flow rates of 5 mL min<sup>-1</sup> and the glass digestion reaction coil above 500 cm, the digestion reaction is virtually complete. Thus, a 500-cm long glass digestion reaction coil (L1) was chosen.

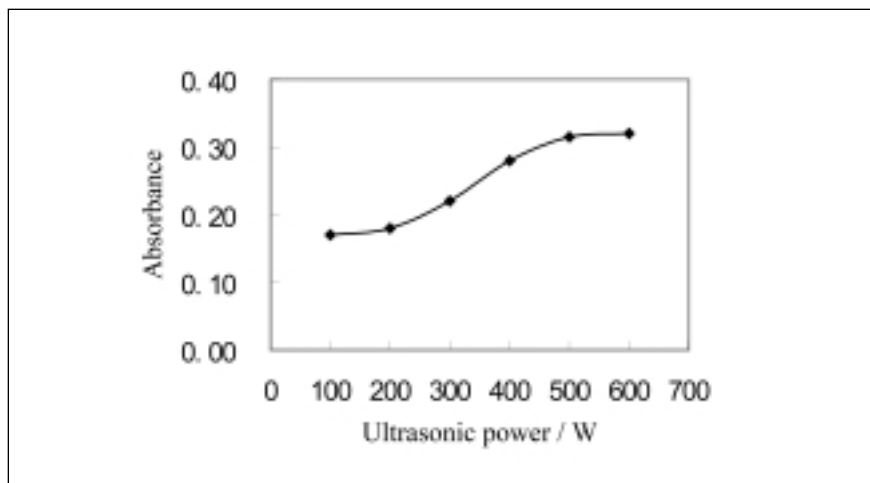


Fig. 3. The effect of ultrasonic power on sample digestion.

Potassium permanganate as an oxidizing reagent (rather than potassium dichromate) is more suitable in the FIA system for the determination of COD because it has a faster and higher oxidation ability and requires milder conditions such as in acidity. The experimental results showed that a potassium permanganate solution of  $2.0 \times 10^{-3}$  mol L<sup>-1</sup> provides complete oxidation digestion of the sample.

#### Optimization of Elution Condition

The elution variables studied are type, concentration and flow rate of eluent, elution time, and mode.

The experimental results of hydrochloric acid, nitric acid, sodium chloride, and ammonium nitrate showed that hydrochloric acid was the best eluent due to its speed of elution and height of peak absorbance signal. The concentration of hydrochloric acid was tested ranging from 0.5–4.5 mol L<sup>-1</sup>. The height of peak absorbance signal increased with an increase in hydrochloric acid concentration up to 3.0 mol L<sup>-1</sup>; above that amount it remained constant. The eluent chosen was 3.0 mol L<sup>-1</sup> of hydrochloric

acid. The signal came back to baseline when the elution with 3.0 mol L<sup>-1</sup> of hydrochloric acid was run for 120 s.

Increasing the flow rate of the eluent would be advantageous to the elution process, but not beneficial to FAAS measurement. The optimum flow rate chosen was 5 mL min<sup>-1</sup>. The mode of reverse elution was the same as reported in our previous study (25).

#### Performance for COD Determination

Under optimum experimental conditions, the absorbance varies linearly with the concentration of COD in the range of 3–300 mg L<sup>-1</sup>, and fits the equation:  $A = 0.00296C + 0.0185$  ( $r = 0.997$ ). The detection limit (DL) of 1 mg L<sup>-1</sup> was calculated as three times the standard deviation of the absorbance for seven injections of the blank. The precision of the method obtained for nine samples containing 30 mg L<sup>-1</sup> of COD was 2.7%, expressed as the relative standard deviation. The analytic throughput was found to be 24 samples per hour.

A lower DL value in comparison to the results from microwave digestion and FAAS detection (13,14) means that ultrasound-assisted digestion is more efficient than microwave digestion despite the milder conditions such as lower acid concentration and lower temperature.

### Interferences

Chlorides cause the most important interferences in COD determination when potassium permanganate or potassium dichromate are used as the oxidizing reagent, since these can also be oxidized. Usually, the way of solving this problem is by adding  $\text{HgSO}_4$  to the sample. The method developed by Hejzlar et al. (19) tolerates chloride concentrations up to  $600 \text{ mg L}^{-1}$  by adding an excess of Cr(III). Korenaga et al. (6) reported that when Ce(IV) is used as the oxidant, as high as  $30,000 \text{ mg L}^{-1}$  of chloride can be tolerated without adding  $\text{HgSO}_4$ . In our study, the interference from chloride was investigated for the determination of  $100 \text{ mg L}^{-1}$  COD. The results listed in Table I show that up to  $1000 \text{ mg L}^{-1}$  of chloride can be tolerated without adding  $\text{HgSO}_4$ .

When using ultrasonic digestion with on-line ion exchange separation and FI-FAAS for the determination of COD, another problem to be considered is that a too high cation concentration in a sample might affect the adsorption of  $\text{Mn}^{2+}$  on micro-column (B). To avoid this interference, the sample was first passed through cation exchange micro-column (A) before reaction with the oxidizing agent.

**TABLE I**  
**Effect of Chloride Concentration on COD Determination**

COD (mg L <sup>-1</sup> )	Cl <sup>-</sup> (mg L <sup>-1</sup> )	A	COD (found) (mg L <sup>-1</sup> )	Error (%)
100	0	0.314	99.8	-0.2
100	50	0.310	98.5	-1.5
100	100	0.317	100.8	0.8
100	500	0.319	101.5	1.5
100	1000	0.321	102.2	2.2
100	5000	0.343	109.6	9.6
100	10,000	0.389	125.2	25.2

**TABLE II**  
**Results of COD Determination in Real Samples**

Sample	COD (mg L <sup>-1</sup> ) <sup>a</sup>		Error (%)
	Proposed Method	Standard Method	
Well Water	11.1	11.6	-4.3
River Water	47.2	46.3	1.9
Pool Water I	84.1	85.9	-2.1
Pool Water II	49.2	48.9	0.6

<sup>a</sup> Average of three determinations.

### Application

To investigate the applicability of the method described to real samples, the COD was determined in well, river, and pool water samples. After filtering, each sample was analyzed directly and the results are given in Table II. Also listed are the results obtained by the conventional and standard methods with potassium dichromate. Application of the statistical *t* test assured that the results of both methods shows no significant difference up to a confidence level of 95%.

### CONCLUSION

An ultrasound-assisted digestion method for the COD determination combined with a flow injection system is described in which  $\text{Mn}^{2+}$  produced by the reduction of  $\text{MO}_4^-$  is separated on-line with a cation exchange micro-column and determined by FAAS. This method proves to be an effective way for the determination of COD and offers lower digestion acidity, shorter digestion time, higher throughput, lower detection limit and interference, simpler operation, and better precision in comparison to other reported methods. It would be desirable to investigate the applicability of this approach further by applying it to the analysis of different types of water samples, for using it in the process control of wastewater treatment, and for quality management of environmental waters.

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