Introduction of electromagnetic induction heating technique into on-line chemical oxygen demand determination

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A flow injection system incorporating electromagnetic induction heating oxidation for on-line determination of chemical oxygen demand (COD) was proposed. The procedure utilised electromagnetic induction heating instead of conventional reflux heating, with acidic potassium dichromate acting both as an oxidant and as a spectrometric reagent. The elevated temperature and pressure inside the reaction coil contributed to the improvement of on-line sample oxidation, and hence, sample oxidation time was reduced to *ca.* 8 min (as compared to 2 h required for conventional method). The sampling frequency was $10\,h^{-1}$, along with a quantification limit of $4.0\,mg\,L^{-1}$ COD and a linear range of 4–$200\,mg\,L^{-1}$ COD (potassium hydrogen phthalate, $r = 0.9958$). Relative standard deviation was evaluated to be 3.5% at $100\,mg\,L^{-1}$ COD and the results were comparable to those obtained by the standard method.

Keywords: pressurised electromagnetic induction heating; chemical oxygen demand; flow injection; spectrophotometry

1. Introduction

Chemical oxygen demand (COD) is a widely used parameter for understanding the pollutional level of water and wastewater. The determination of COD involves measuring the equivalent amount of oxygen required to decompose the organic matter in a sample with a strong chemical oxidant such as potassium dichromate [1,2], potassium permanganate [3], ceric sulphate [4], etc. Among them, potassium dichromate has been found to be the most suitable oxidant since it is capable of oxidising the carbonaceous matter completely to carbon dioxide and water [5] and it is used in many standard methods endorsed by several international bodies [6–8]. These standard methods are widely used but limited by long reflux times (approximately 2–2.5 h), volatilisation of organics, and tedious manual procedures with the potential for error. In view of these drawbacks, an ideal method suitable for determination of COD should be quick, simple, cheap and as effective as the standard method in oxidising water samples.

In recent years, a great deal of effort has been devoted to the development of other suitable methods. Zhang *et al.* proposed a flow injection (FI) flame absorption spectrometry (FI-FAAS) system for rapid determination of COD [9]. In their work, ultrasonic wave was employed to advance sample digestion by potassium permanganate

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and the generated Mn (II) was separated from Mn (VII) with a cation exchange column. Recently, the photocatalytic decomposition of organic pollutants in water has received much attention. A FI manifold incorporating UV-photocatalytic oxidation for the determination of COD in fresh water was reported by Dan et al. [10]. Kim et al. also utilised FI-based photocatalysis of organic compounds and the change in the dissolved oxygen was detected by amperometric analysis [11]. Su et al. established a novel on-line method based on the marriage of UV photolysis with chemiluminnescence detection for the determination of COD [12]. Microwave heating is another powerful technique known for rapid digestion in COD determination and a number of techniques have been published up to now. A mercury-free microwave method for the COD analysis of sewage samples was related by Axen and Morrison [13]. As they reported, the oxidation time was reduced dramatically (down to 2 min) and lower sulphuric acid concentrations were required for full sample oxidation under pressurised microwave conditions which reduced interference from chloride oxidation to a tolerable level. Cuesta et al. combined microwave digestion with flame atomic absorption spectrometry (FAAS) detection of non-reduced Cr(VI) for the evaluation of COD [14,15]. A focused microwave heating system featuring temperature control was designed by Ramon et al. for the determination of COD in wastewater [16]. However, high initial cost of the equipment, safety limitations and high energy consumption of microwave heating should be mentioned.

Electromagnetic induction heating (EMIH) has been shown to be effective in processing food, drink, wood, etc., to save energy and reduce processing time [17]. It was a clean, fast and easy controllable heating method and has been proven to be an interesting alternative to conventional off-line digestion or microwave heating for sample preparation [18–22]. Owing to the heating energy concentrating just in a thin layer beneath the surface of the heated ferromagnetic material, it was possible to obtain high heating efficiency and heating rate. Our previous work has successfully applied it to on-line digestion of sample for atomic fluorescence spectrometry determination of mercury in edible seaweeds [18], fish samples [19], and cigarette smoke [20]. With regard to its application to COD determination, no work has been reported to the best of our knowledge.

The objective of the present study was to introduce the EMIH technique to COD determination. An on-line pressurised oxidation FI system for COD evaluation was developed. The heat generated inside the solution was beneficial for the efficient transfer of energy and, hence, there was reduced energy consumption. In the proposed method, a back pressure coil (BPC) was installed downstream. When samples flowed through the EMHC, on-line oxidation lasts circa 8 min under approximately 145°C reaction temperature and 0.44 MPa manifold pressure, and the corresponding heating power was just 40 W. The pressure built up in-line contributed not only to sample oxidation but also to reduction of bubble formation. By on-line coupling the pressurised EMIH system to a spectrophotometer, the proposed method could be applied to the determination of COD successfully.

2. Experimental

2.1 Reagents and solutions

The chemicals used in this work were analytical grade and purchased from Sinopharm Group Chemical Reagent Co. (Shanghai, China), unless otherwise noted.

A $0.004 \, \text{mol} \, \text{L}^{-1}$ acidic potassium dichromate solution was prepared by dissolving $1.2258 \, \text{g} \, K_2Cr_2O_7$ (dried at about 105°C for 2 h) in 1000 mL of $5.4 \, \text{mol} \, \text{L}^{-1}$ sulphuric acid. Previously, Ag_2SO_4 (Nanjing Chemical Reagent Co.) had been added to the concentrated H_2SO_4 in the proportion of $3.0 \, \text{g} \, Ag_2SO_4$ per 100 mL of H_2SO_4 (i.e. $4.5 \, \text{g} \, \text{L}^{-1}$ after merging with the carrier) for catalysing. The acidic potassium dichromate solution was renewed every month. Standard solution of potassium hydrogen phthalate (KHP) with a theoretical COD value of $1000 \, \text{mg} \, \text{L}^{-1}$ was prepared by dissolving 0.4251 g KHP (dried at about 105°C for 2 h) in 500 mL deionised water. A $1000 \, \text{mg} \, \text{L}^{-1}$ chloride solution was prepared with sodium chloride.

All solutions were degassed for 20 min by an AS206B ultrasonic bath at high power level prior to use.

2.2 *Instrumentation and analytical procedure*

The FI system for the determination of COD with EMIH oxidation is shown in Figure 1. The system was mainly composed of six parts: self-made high-frequency induction heating power supply (HFPS), electromagnetic induction heating coil (EIHC), electromagnetic heating column (EMHC), a 0.3 mm i.d. × 3.5 m length BPC, a IFIS-C peristaltic pump (Xi'an Ruimai Electronic Technology Co., Xi'an, China) as well as a model 756 PC spectrophotometer equipped with a flow cell (Tianjin Tuopu Instrument Co., Tianjin, China).

The HFPS, EIHC and EMHC used in this work were similar to our previous work [18]. The EIHC (10 mm i.d. × 20 mm o.d. × 80 cm length) was fabricated by coiling 5 mm o.d. copper tube and connected to the HFPS. The EMHC was made with a polytetrafluoroethylene (PTFE) outer tube (4.2 mm i.d. × 9.2 mm o.d. × 80 cm length). Seven iron wires (0.8 mm diameter × 79 cm length) sealed in thinner PTFE tubing (0.8 mm i.d. × 1.4 mm o.d. × 80 cm length) were filled in the PTFE outer tube compactly. EMHC was inserted into the cavity of EIHC.

A high-precision pressure gauge (Xi'an High-precision Instrument Factory, Xi'an, China) and a thermocouple were respectively used for pressure and temperature measurement. An AS206B ultrasonic bath (Tianjin Automatic Science Instrument Co., Tianjin, China) was employed for degassing all the solutions.
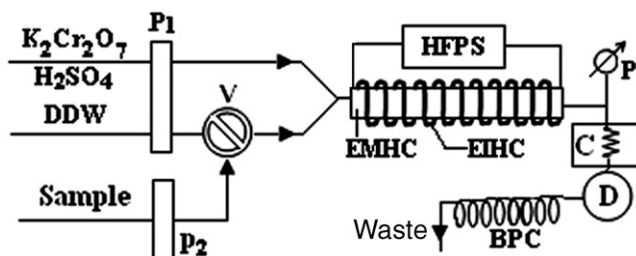

Figure 1. The schematic diagram of the FI manifold for the determination of COD. P_1 and P_2, peristaltic pump; V, rotary injection valve; P, pressure gauge; HFPS, high-frequency induction heating power supply; EMHC, electromagnetic heating column; EIHC, electromagnetic induction heating coil; D, spectrophotometer; C, cooling coil; BPC, back pressure coil.

Before HFPS was started, air was expelled from EMHC by pumping degassed deionised water (DDW) and it was ensured that EMHC was full of water, because the high temperature of iron wires would damage EMHC otherwise. Prior to sample detection, DDW was pumped at a flow rate of $0.15\,mL\,min^{-1}$ for 12 min to reach the equilibrium pressure when heating power was fixed to 40 W. A $0.15\,mL\,min^{-1}$ oxidant reagent stream containing $0.004\,mol\,L^{-1}$ $K_2Cr_2O_7$ and $5.4\,mol\,L^{-1}$ H_2SO_4 was merged with a $0.15\,mL\,min^{-1}$ water carrier. The sample injected into water carrier was oxidised on-line in EMHC followed by flowing through a 0.8 mm i.d. × 0.5 m length cooling coil that was placed in an ice bath. Then, the reduction in dichromate absorbance (ΔA) due to oxidation of the organic compounds was measured at 445 nm.

A PTFE protective tube was placed outside EIHC throughout the experiment for the purpose of safety.

2.3 Sample preparation

The water sample (100 mL) was stabilised with 0.05 mL concentrated H_2SO_4 and stored in the refrigerator at 4°C as soon as this was collected. The addition of H_2SO_4 and the storage at low temperature decreased microbial activity and in this way the samples could be stored for more than 4 weeks without any appreciable change in their COD values. After 5 weeks, the COD value increased by 7% owing to the biological decomposition [23]. The filtration of samples by membrane filter or homogenisation is not essential in our work and the reproducibility of the obtained results was satisfactory. It is worthy of note that turbid samples would require filtration as suggested in reference [1].

2.4 Standard titrimetric method for COD determination

The National Standards of the People's Republic of China [24], which is comparable to other international standards methods [6–8], was used. Water sample (20 mL) was mixed with 0.4 g $HgSO_4$ in a 250 mL round-bottomed flask, then 10 mL of $0.04\,mol\,L^{-1}$ $K_2Cr_2O_7$ was added, followed by a mixture of $18\,mol\,L^{-1}$ H_2SO_4 and $0.03\,mol\,L^{-1}$ Ag_2SO_4 (30 mL). Therefore, the final H_2SO_4 concentration was $9\,mol\,L^{-1}$. The sample was digested and refluxed for 2 h and, after cooling and rinsing with deionised water, residual dichromate was back-titrated with $0.1\,mol\,L^{-1}$ $(NH_4)_2Fe(SO_4)_2$ using ferroin as an indicator. COD value was calculated from the differences in titration values between the sample and blank.

3. Results and discussion

3.1 Design of the on-line oxidation system

First, both the sample oxidation and sample zone extension were taken into account for choosing an appropriate EMHC dimension. Larger EMHC diameter causes obvious dispersion of the sample plug along the EMHC of sample zone and the decrease of ΔA, whereas EMHC with small diameter could not ensure sufficient sample oxidation time at a certain flow rate. Consequently, a 4.2 mm i.d. × 9.2 mm o.d. PTFE tube compactly packed with seven 1.4 mm o.d. PTFE-coated iron wires was employed as the EMHC and a 10 mm i.d. × 20 mm o.d. EIHC was chosen accordingly.

Table 1. The RSD for different EMHC length ($n = 6$).

BPC length (cm)	RSD (%)
40	19.2
60	9.5
80	4.1
100	3.7
120	4.0

Table 2. The equilibrium pressure for different BPC length.

BPC length (m)	Equilibrium pressure (Mpa)
0.5	0.20
1.0	0.31
1.5	0.38
2.0	0.41
2.5	0.43
3.0	0.44
3.5	0.44
4.0	0.44

The influence of EMHC length was investigated from 40 to 120 cm. The ΔA increased from 0.015 to 0.030 along with EMHC length up to 100 cm, and then peaks became broader with no obvious ΔA increase. In addition, the relative standard deviation (RSD) for six repetitive determinations of $100 \, mg \, L^{-1}$ COD (as KHP) at different EMHC length were listed in Table 1. Thus, an EMHC of 80 cm length was selected as a compromise between sensitivity and reproducibility.

Higher equilibrium pressure built up in the manifold increased the boiling point of oxidant reagent and hence allows the solution to reach a higher temperature for better sample oxidation at a relative lower H_2SO_4 concentration. Similar reports could be found elsewhere [13,25]. Equilibrium pressure of EMHC was significantly influenced by the size of BPC. The results indicated that equilibrium pressure obviously increased as diminishing the inner diameter of BPC. In our work, the PTFE coil with inner diameters less than 0.30 mm was not taken into consideration to avoid tubing blockage. Hence, a 0.35 mm i.d. tubing was employed. The equilibrium pressure also enlarged with increasing the BPC length until 3 m and then levelled off at $0.15 \, mL \, min^{-1}$ flow rate and 40 W heating power (Table 2). As a result, a 0.35 mm i.d. $\times$ 3.5 m length BPC was installed just after the flow cell. The pressure of *ca.* 0.44 MPa built up in-line contributed to both the improvement of on-line sample oxidation and the reduction of bubble formation. Nevertheless, a few bubbles still existed in the stream under the pressure. This problem could be solved by employing carefully degassed solution as Appleton and Tyson suggested [26].

3.2 *Selection of on-line oxidation parameters*

The response of equilibrium pressure and temperature to heating power was investigated in detail. It was found that temperature and equilibrium pressure increased gradually with
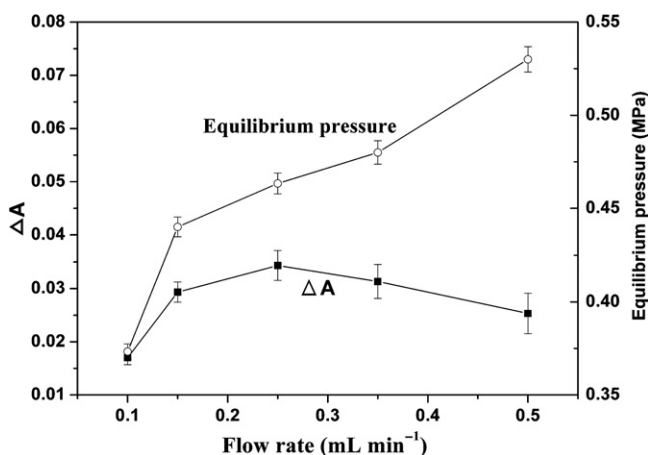
Figure 2. Effect of flow rate on ΔA and equilibrium pressure. COD, $100 \, mg \, L^{-1}$ KHP; heating power, 40 W; oxidant, $4 \times 10^{-3} \, mol \, L^{-1}$ $K_2Cr_2O_7 + 5.4 \, mol \, L^{-1}$ H_2SO_4; sample volume, $450 \, \mu L$.

increasing the heating power when the flow rates of oxidant reagent and DDW carrier were both fixed to $0.15 \, mL \, min^{-1}$. Additionally, the influence of temperature on ΔA was investigated in detail. Temperatures below $115°C$ got poor sensitivity, and between 115 and $150°C$ gave constant ΔA values. While the temperature was over $150°C$, a few bubbles formed in the manifold and led to distorted peak shapes and an impaired ΔA value. Therefore, the power was set to 40 W and the corresponding reaction temperature and equilibrium pressure were $145°C$ and $0.44 \, MPa$, respectively.

Figure 2 shows the variation of ΔA value and equilibrium pressure over flow rates when $100 \, mg \, L^{-1}$ COD KHP solution was processed. The equilibrium pressure and analytical throughput could be enhanced by increased flow rate. However, an attempt to reduce the analytical time by increasing the flow rates of oxidant reagent and DDW carrier led to increased reagent consumption, reduced baseline stability as well as shortened oxidation time. On the other hand, much lower flow rate resulted in severe peak broadening and reduced ΔA values. Consequently, the flow rate of $0.15 \, mL \, min^{-1}$ was selected as a reasonable compromise between precision and sensitivity, and the corresponding reaction time in EMHC was about 8 min. The ration of the flow rates of oxidant reagent and DDW carrier stream was maintained at $1:1$ to ensure efficient mixing and a period of 12 min was needed to reach $0.44 \, MPa$ equilibrium pressure.

The influence of sample injection volume on ΔA and analytical throughput was investigated in the range $300–900 \, \mu L$ (Figure 3). As expected, ΔA increased with injection volume. At the same time, larger sample volume resulted in a lower analytical throughput and reduced linear calibration range [26]. Take into consideration of above-mentioned reasons, a sample volume of $450 \, \mu L$ was selected for further study.

The selection of time interval between adjacent samples was carried out when two samples were injected. As shown in Figure 4, sample peaks could not be separated as time intervals ranged from 1 min to 4 min. When time intervals were equal or more than 6 min, separated absorption peaks could be obtained and the individual peak height was identical with that obtained by a single sample injection. Hence, samples were injected at 6 min intervals when $450 \, \mu L$ samples were introduced into a $0.15 \, mL \, min^{-1}$ DDW carrier stream.
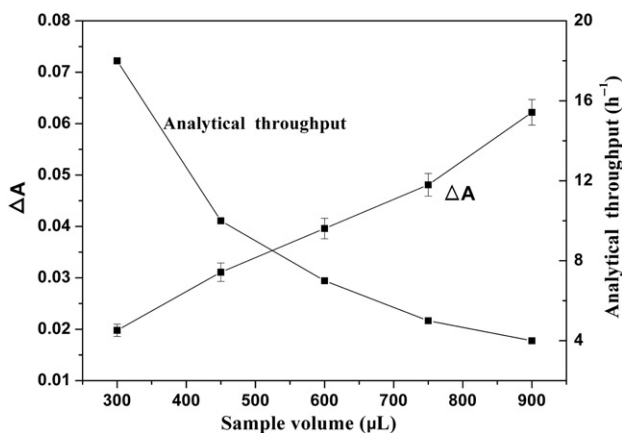
Figure 3. Effect of sample volume on (1) ΔA and (2) analytical throughput. COD, 100 mg L^{-1} KHP; heating power, 40 W; oxidant, 4×10^{-3} mol L^{-1} K$_2$Cr$_2$O$_7$ + 5.4 mol L^{-1} H$_2$SO$_4$; flow rate, 0.15 mL min^{-1}.
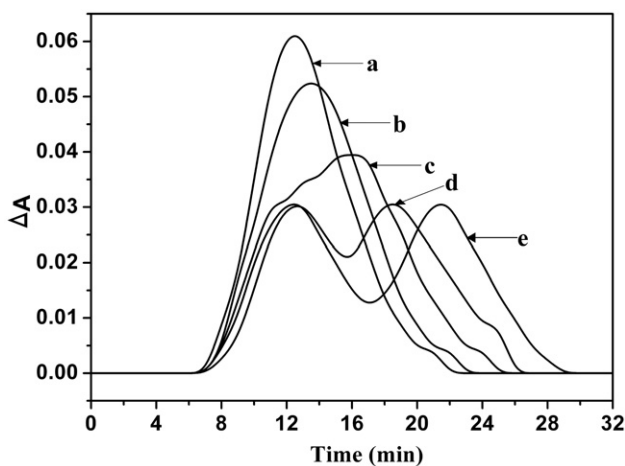
Figure 4. Influence of time intervals (a, 1 min; b, 2 min; c, 4 min; d, 6 min; e, 8 min) on ΔA. COD, 100 mg L^{-1} KHP; heating power, 40 W; oxidant, 4×10^{-3} mol L^{-1} K$_2$Cr$_2$O$_7$ + 5.4 mol L^{-1} H$_2$SO$_4$; flow rate, 0.15 mL min^{-1}; sample volume, 450 μL.

The influence of H$_2$SO$_4$ concentration on ΔA was investigated over the range 10–50% (v/v). It was found that ΔA increased from 0.012 to 0.028 with the increase of H$_2$SO$_4$ concentration from 10% to 25% (v/v) and then remained constant. Accordingly, a 30% (v/v) H$_2$SO$_4$ acidified potassium dichromate solution was employed in our work, i.e. the selected H$_2$SO$_4$ concentration was 5.4 mol L^{-1}.

3.3 *Chloride ion interference in COD determination*

Chloride could be oxidised by the dichromate and would result in a positive interference in COD determination. The results of chloride (0–2000 mg L^{-1}) interference on the
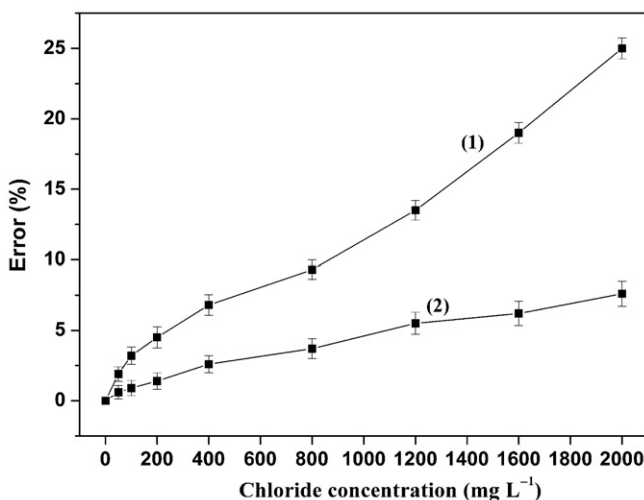
Figure 5. Effect of chloride concentration on COD determination: (1) without addition of $HgSO_4$ (2) with addition of $10\,g\,L^{-1}$ $HgSO_4$. COD, $100\,mg\,L^{-1}$ KHP; heating power, $40\,W$; oxidant, $4 \times 10^{-3}\,mol\,L^{-1}$ $K_2Cr_2O_7$ + $5.4\,mol\,L^{-1}$ H_2SO_4; flow rate, $0.15\,mL\,min^{-1}$; sample volume, $450\,\mu L$.

determination of $100\,mg\,L^{-1}$ COD (as KHP) are shown in Figure 5. Negligible interferences were observed for solutions with chloride concentrations less than $200\,mg\,L^{-1}$; 200 to $800\,mg\,L^{-1}$ chloride gave rise to slight interference, and these errors could be tolerable in many situations; higher than $1200\,mg\,L^{-1}$ chloride interfered severely with COD measurement. Usually, $HgSO_4$ was selected to mask chloride. The concentration of $HgSO_4$ required to remove the interference is related to the concentration of chloride in the sample. A $HgSO_4/Cl^{-1}$ ration 10 : 1 (w/w) can mask chloride concentrations up to $2000\,mg\,L^{-1}$, as recommended by the standard method [8]. As shown in Figure 5, the interference of $2000\,mg\,L^{-1}$ chloride can be reduced to acceptable level by employing $10\,g\,L^{-1}$ $HgSO_4$ in the present study. Samples were merged with $HgSO_4$ prior to injection into the carrier. Since $HgSO_4$ is extremely toxic, an appropriate amount only should be incorporated into the sample when necessary.

3.4 *Analytical figures of merit*

Under the recommended experimental conditions, the linear graph corresponded to the equation $\Delta A = 3.23 \times 10^{-4}\,C - 1.20 \times 10^{-3}$ with the relation coefficient $r = 0.9958$, where ΔA is the decrease of the absorbance caused by the standard solution (or sample) and C is the COD expressed in $mg\,L^{-1}$. The ΔA varies linearly with the concentration of COD in the range 4–$200\,mg\,L^{-1}$, hence, water samples with higher COD value need appropriate dilution before analysis. The limit of quantification of $4.0\,mg\,L^{-1}$ was calculated as ten times the standard deviation of the absorbance for nine injections of the blank and RSD was evaluated to be 3.5% at $100\,mg\,L^{-1}$ COD ($n = 10$). The analytical throughput was about 10 samples per hour. These values were comparable with those previously reported FI methods and the comparison of the main analytical parameters were summarised in Table 3.

Table 3. Comparison of main analytical parameters in FI methods for COD determination.

Method	Oxidisation condition	Reaction time (min)	Sampling frequency (h^{-1})	LOD ($mg L^{-1}$)	RSD (%) ($mg\,COD\,L^{-1}$)	Recovery (%)	Ref.
			Analytical parameters				
Corn oil bath	$K_2Cr_2O_7$ (120°C)	20	15	5	0.4 (126)	–	[1]
UV irradiation	$KMnO_4$ (254 nm)	1.5	30	0.5	2.7 (5) 1.21 (10)	83.0–111.0	[10]
UV photo-catalytic	TiO_2 (365 nm)	–	3	1	4.4 (5.9 $mg\,O_2\,L^{-1}$)	–	[11][a]
Microwave	$K_2Cr_2O_7$ (662 W)	7	50	7	4.1 (100) 8.6 (76.5)	–	[14]
EMIH	$K_2Cr_2O_7$ (40 W)	8	10	4.0[b]	3.5 (100)	84–108	This work

Notes: [a]Anal. Chem. **74**, 3858 (2002).
[b]Calculated as ten times the standard deviation of the absorbance for nine blank value.

Table 4. Analytical results of COD in freshwater samples ($n = 5$).

Sample	Standard method COD ($mg L^{-1}$) Found[a]	Proposed method COD ($mg L^{-1}$) Found[a]	Added	Reclaimed[a]	Recovery %	t-Test[b]
Chaohu lake	40.1 ± 1.2	37.5 ± 2.0	50	91.3 ± 3.7	108	2.49
Baotu spring	9.9 ± 0.4	10.4 ± 0.5	10	18.8 ± 0.5	84	1.74
Local river	26.0 ± 1.3	24.6 ± 1.8	50	70.9 ± 4.1	93	1.07
Laboratory wastewater	75.5 ± 2.7	71.3 ± 2.2	50	115.6 ± 5.0	89	2.72

Notes: [a]Results given are obtained as averages of five measurements ± SD.
[b]Theoretical value at 95% confidence level is 2.78.

3.5 *Application to the analysis of real samples*

Freshwater samples obtained from Chaohu lake (Anhui, China), Baotu spring (Jinan, China), a local river (Hefei, China) as well as wastewater collected from the sewage outlet of our laboratory building were analysed. Table 4 lists the COD values obtained by the proposed method and those obtained by the standard method [24]. There was no statistical difference according to a paired *t*-test applied at 95% confidence level. The reliability of the developed method was also tested with recovery experiments by adding appropriate KHP into samples and the obtained recoveries ranged from 84% to 108% (Table 4).

The proposed method was also used for measuring COD of plant effluents collected from three food factories and two textile industries located in Hefei area. Due to the presence of less readily oxidised organic pollutants, the COD values obtained by the proposed FI method were about 70% of those obtained by the standard method [24].

To evaluate the correlation of the proposed method with the standard method, 20 wastewater samples from a food factory and 20 wastewater samples from a textile factory taken at two hour intervals between 9:00 and 17:00 from March 21 to March 24 (five samples per day) were analysed. The correlation relationships were $y = 0.68\chi + 5.2$ and $y = 0.73\chi - 6.7$, respectively, for food and textile wastewater samples, where y were the averages of three determination results obtained by the proposed method and χ were the averages of two determination results obtained by the standard method. The correlation coefficients were 0.96 and 0.97, respectively.

4. Conclusion

It is the first time that electromagnetic induction heating technique was introduced to COD evaluation to the best of our knowledge. The use of pressurised electromagnetic induction heating in conjunction with flow injection and spectroscopy detection has been proven to be effective in the determination of COD. On-line sample oxidation was achieved at 145°C reaction temperature and 0.44 MPa manifold pressure within *circa* 8 min. Due to the heating energy generated inside the sample solution and concentrated just in a thin layer beneath the surface of heated material [21], the proposed method reduced energy consumption as compared to the conventional reflux heating as well as the corn oil bath heating and microwave heating mentioned in Table 3 [1,14]. Additionally, the proposed method eliminated the long reflux time normally required. The combination of FI with spectroscopy detection offered simpler and safer operation. Besides, the proposed method has the advantages of less reagent consumption, reduced external contamination as well as lower cost.

The proposed method provided good comparison results with respect to the standard method for the analysis of relative freshwater samples and offered valid reference to plant effluents measurement (the values obtained by the developed method gave oxidation ratios of about 70% of those obtained by the standard method). It provided a promising alternative approach for on-line COD monitoring.

Acknowledgement

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