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Flow injection spectrophotometric determination of formaldehyde based on its condensation with hydroxylamine and subsequent redox reaction with iron(III)–ferrozine complex

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ABSTRACT

A flow injection (FI) spectrophotometric method is proposed for the determination of low concentration of formaldehyde (HCHO) in liquid media. It is based on the condensation of HCHO with hydroxylamine sulfate, followed by the reduction reaction of iron(III)–ferrozine complex with the residual hydroxylamine to form a purple iron(II)–ferrozine complex (λ_{max} = 562 nm). In the first reaction, hydroxylamine decreases proportionally to the concentration of HCHO, and therefore the produced purple iron(II)–ferrozine complex decreases with increasing HCHO (a negative FI peak is obtained). The detection limit (S/N = 3) was 1.6 μg L^{-1}. The method can be applied to the determination of HCHO in industrial wastewater.

1. Introduction

Formaldehyde (HCHO) is widely used as a fundamental building block for organic synthesis in industry, e.g. urea formaldehyde resin, melamine resin, phenol formaldehyde resin, and also it is extremely useful for disinfection in clinical field. However, exposure to HCHO in higher concentration can cause well-known effects as irritation of the eyes and upper respiratory tract, burning sensations in the mucous membrane and so on. To prevent significant sensory irritation in the general population, an air quality guideline value of 0.1 mg m^{-3} (0.08 ppmv) as a 30 min average is recommended by the World Health Organization [1].

On the other hand, discharge of HCHO in hydrosphere should be also paid attention. Japanese government partly revised environmental quality standards for water pollution in 2003, and HCHO was added as a monitoring substance in living environment items [2]. The guideline value is equal to or less than 1 mg L^{-1} in rivers and lakes. Industrial wastewater is discharged into water environment, so it must be strictly controlled.

Murai et al. [3] reported a sensitive spectrophotometry for HCHO in rainwater by membrane solubilization technique. In this batch method, HCHO was converted into a blue cationic dye with 3-methyl-2-benzothiazolinone hydrazone (MBTH), and the dye was retained on a membrane filter as an ion-associate with tetraphenylborate anion, followed by dissolving the filter in 2-methoxyethanol containing sulfuric acid to measure the absorbance at 670 nm. This method is sensitive, however such manual procedure is time consuming and tedious.

Utilization of flow-based analysis techniques is attractive for assembling rapid, reproducible and automated analytical systems for HCHO determination. MBTH method was introduced into a flow injection analysis (FIA) system for the spectrophotometric determination of HCHO in indoor and ambient air [4]. It is well-known that Hantzsch reactions are useful for the determination of HCHO [5]. A lot of spectrophotometric or fluorometric FIA methods based on Hantzsch reactions have been reported for the determination of HCHO in atmosphere [6], indoor air [7], human exhaled breath [8], natural waters [9–11] and food [12]. However, these methods have not been applied to industrial wastewater analysis.

Nakano et al. [13] developed a monitoring tape for gaseous HCHO, based on its condensation with hydroxylamine sulfate where sulfuric acid was liberated. The porous cellulose tape was impregnated with hydroxylamine sulfate and methyl yellow (a pH indicator), so that the color change could be observed by the liberated sulfuric acid. However this method has not been applied to water samples.

We found recently that the residual hydroxylamine in the above mentioned condensation reduced iron(III) to iron(II) in the presence of 1,10-phenanthroline (phen) to produce a red iron(II)–phen complex [14]. Since the decrease in the absorbance of the complex was proportional to the concentration of HCHO, we developed a spectrophotometric FIA method for HCHO determination by

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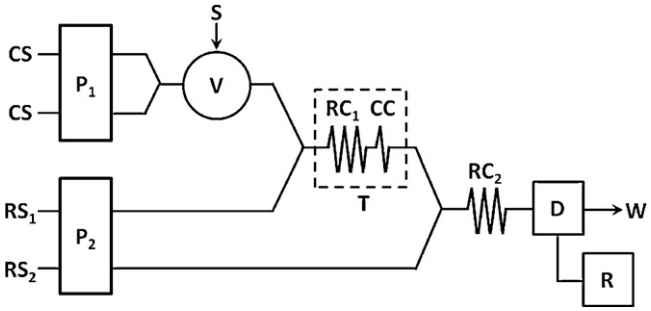

Fig. 1. Schematic flow diagram of the FIA system. CS, carrier solution (H_2O); RS_1, 1.0×10^{-5} M hydroxylamine sulfate; RS_2, mixed solution of 1.6×10^{-4} M iron(III), 8.0×10^{-4} M ferrozine and 0.1 M acetate buffer (pH 5.0); V, 6-way valve; S, formaldehyde standard/sample (200 μL); P_1 and P_2, double plunger pumps (0.3 mL min^{-1} each pump); *T*, temperature control system (90 °C); D, spectrophotometer (562 nm); RC_1, 0.5 mm i.d. ×8 m; CC, 2 m; RC_2, 0.5 mm i.d. ×6 m; R, recorder and W, waste.

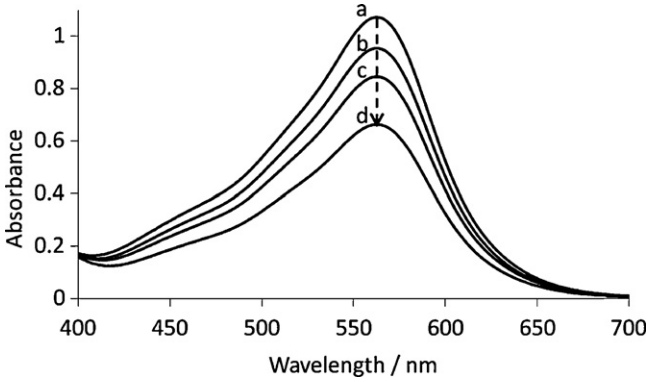

Fig. 2. Absorption spectra of the reaction product. Formaldehyde concentration (mg L^{-1}): (a) 0; (b) 0.25; (c) 0.50 and (d) 1.00. $C_{hydroxylamine\ sulfate}$, 2.0×10^{-5} M; $C_{iron(III)}$, 8.0×10^{-5} M; $C_{ferrozine}$, 5.0×10^{-4} M; $C_{acetate\ buffer}$ (pH 5.0), 0.1 M.

monitoring the residual hydroxylamine using iron(III)–phen complex. In the present work, we investigated other two ligands such as 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) and ferrozine which have larger molar absorptivity compared with phen. As a result, a highly sensitive FIA method based on the condensation followed by the reduction reaction of iron(III)–ferrozine complex has been proposed.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and were used without further purification. Deionized water used to prepare solutions was obtained from an Advantec GSH-200 apparatus.

A HCHO solution (37% HCHO, 8% methanol, Nacalai Tesque, Kyoto) standardized by iodometry was used to produce a 1% w/w (10,000 mg L^{-1}) HCHO standard solution. The solution was diluted with water before use.

A hydroxylamine sulfate stock solution (1.0×10^{-2} M) was prepared by 0.16 g of hydroxylamine sulfate (Wako Pure Chemical Industries, Osaka) in 100 mL of water. Working solution of hydroxylamine was prepared by diluting the stock solution with water.

An iron(III) stock solution (2.0×10^{-3} M) was prepared by dissolving 0.0964 g of ammonium iron(III) sulfate dodecahydrate in 100 mL of 0.2 M hydrochloric acid.

1.0 M sodium acetate was mixed with 1.0 M acetic acid solution to obtain an acetate buffer solution at pH 5.0.

A mixed solution containing 1.6×10^{-4} M iron(III), 8.0×10^{-4} M ferrozine (Dojindo Laboratories, Kumamoto, the trade name is PDTS) and 0.1 M acetate buffer at pH 5.0 was daily prepared. The mixed solution constituted RS_2 referred to in Section 2.2.

TPTZ was purchased from Dojindo Laboratories, and it was mixed in the reagent solution (RS_2) in place of ferrozine (eventually this ligand has not been chosen).

2.2. Apparatus and procedure

Fig. 1 shows the manifold of the FIA system of this work. Flow rates of two double plunger pumps (Dual Pump 201 and Intelligent Pump 301 M, FLOM, Tokyo) were set at 0.3 mL min^{-1}, respectively (0.15 mL min^{-1} each channel). The HCHO condensation with hydroxylamine occurred in a temperature control system (S-3850, Soma Optics) which consisted of a heated reaction coil at 90 °C (RC_1, 0.5 mm i.d., 8 m long) and a cooled reaction coil at 25 °C (CC, 0.5 mm i.d., 2 m long) attached to a built-in Peltier device. A double beam spectrophotometer (S-3250, Soma Optics, Tokyo) fitted with a flow-through cell (8 μL volume, 10 mm path length) was used for absorbance measurement. The signal was recorded on a recorder (Chino, EB 22005, Tokyo).

An aliquot of HCHO standard/sample (200 μL) injected into a carrier solution of water (CS) merged with 1.0×10^{-5} M hydroxylamine sulfate (RS_1) and with a mixed solution of 1.6×10^{-4} M iron(III), 8.0×10^{-4} M ferrozine and 0.1 M acetate buffer at pH 5.0 (RS_2). The absorbance of the purple colored iron(II)–ferrozine complex was monitored at 562 nm.

3. Results and discussion

3.1. Absorption spectra

HCHO reacts with hydroxylamine sulfate to produce formaldoxime and to liberate sulfuric acid as shown in Eq. (1):

$$2HCHO + (NH_2OH)_2{\cdot}H_2SO_4 \leftrightharpoons 2H_2C{=}NOH + H_2SO_4 + 2H_2O \quad (1)$$

In this reaction, hydroxylamine decreases in proportion to the concentration of HCHO. The residual hydroxylamine reduces iron(III) to iron(II) [15]:

$$(NH_2OH)_2{\cdot}H_2SO_4 + 4Fe^{3+} \rightleftharpoons N_2O + H_2O + 6H^+ + 4Fe^{2+} + SO_4{}^{2-} \quad (2)$$

The produced iron(II) reacts with ferrozine to form a purple iron(II)–ferrozine complex that has an absorption maximum at 562 nm:

$$Fe^{2+} + 3ferrozine^{2-} \rightleftharpoons [Fe(ferrozine)_3]^{4-} \quad (3)$$

Therefore, the decrease in hydroxylamine can be monitored by measuring the decrease in absorbance at 562 nm. Preliminary batchwise study was conducted to obtain absorption spectra of the reaction products as follows. To 1.0 mL of 2.5×10^{-4} M hydroxylamine sulfate in a 10 mL volumetric flask, 0–2.0 mL of 5.0 mg L^{-1} HCHO standard solution was added, followed by adding 2.0–0 mL of water (the volume of the mixed solution was 5.0 mL each). Then, 1.0 mL of 8.0×10^{-4} M iron(III), 1.0 mL of 5.0×10^{-3} M ferrozine and 1.0 mL of 1.0 M acetate buffer (pH 5.0) were added. After diluting to the mark with water, the solution was allowed to stand for 20 min at room temperature. Finally the absorption spectra were measured. As shown in Fig. 2, the absorbance at 562 nm decreased proportionally to the concentration of HCHO.

When an HCHO solution was injected into the carrier solution, the hydroxylamine concentration decreased and consequently the concentration of the produced purple complex became smaller, recording a negative peak for HCHO.

Table 1
The values of Δ absorbance for 0.25 mg L^{-1} formaldehyde using three ligands and characteristics of their iron(II) complexes.

Ligand	Δ Absorbance[a]	ε[b]/L mol^{-1} cm^{-1}	λ_{max}/nm	Composition
Phen[c]	$0.013 \pm 0.000_3$	11,100	510	$[Fe(phen)_3]^{2+}$
TPTZ[d]	$0.026 \pm 0.000_2$	22,600	593	$[Fe(tptz)_2]^{2+}$
Ferrozine	$0.035 \pm 0.000_5$	27,900	562	$[Fe(ferrozine)_3]^{4-}$

[a] Corresponded to the magnitude of the negative peaks ($n = 3$).
[b] Ref. [16].
[c] 1,10-Phenanthroline.
[d] 2,4,6-Tris(2-pyridyl)-1,3,5-triazine.

3.2. Effect of ligand on the sensitivity

In a previous paper [14], we employed an iron(III)–phen complex in order to monitor the residual hydroxylamine which produced a red iron(II)–phen complex. We investigated the effect of ligands such as phen, TPTZ and ferrozine on the sensitivity in this FIA system. The results together with the characteristics of their iron(II) complexes are shown in Table 1. When a solution of iron(III)–ferrozine complex buffered at pH 5.0 was delivered from RS_2, the highest negative peak for HCHO was obtained. The molar absorptivities of iron(II)–phen, –TPTZ and –ferrozine complexes are 1.10×10^4, 2.26×10^4 and 2.79×10^4 L mol^{-1} cm^{-1} [16]. The differences in the sensitivity of our study can be attributable to the difference in the molar absorptivities. We chose ferrozine for the following experiments.

3.3. Optimization study

All reaction parameters were optimized using a 0.25 mg L^{-1} HCHO standard solution. The examined ranges and the chosen optimum conditions except for ferrozine concentration (its dependence is described in the next section) are summarized in Table 2.

3.3.1. Effects of chemicals

The magnitude of negative peak height decreased above 1.0×10^{-5} M hydroxylamine. Only hydroxylamine concentration of 1.0×10^{-5} was needed to obtain a good sensitivity. The sensitivity increased with an increase in iron(III) concentration. However, at iron(III) concentrations higher than 1.6×10^{-4} M, there was higher baseline absorbance caused by higher concentration of iron(II)–ferrozine complex which gave a noisy baseline. Therefore, an iron(III) concentration of 1.6×10^{-4} M was chosen. Ferrozine concentration was also varied, and the result is shown in Fig. 3. The sensitivity increased with increasing ferrozine concentration up to 4.0×10^{-4} M and kept nearly the same sensitivity till 1.2×10^{-3} M. We chose a ferrozine concentration of 8.0×10^{-4} M.

3.3.2. Effect of pH

The sensitivity increased with increasing pH, because liberation of proton during the condensation is reasonably favorable at higher pH. However, at pH higher than 5.0, hydrolysis of iron(III) can be expected. In fact, in our previous study using phen [14], the sensitivity slightly decreased at pH 6.0, and therefore an acetate buffer at pH 5.0 was employed. In the present study, we also chose the same buffer solution at pH 5.0.

Table 2
Examined ranges of reaction parameters and optimum condition.

Parameter	Range	Optimum chosen
[Hydroxylamine]	2.0×10^{-6}–8.0×10^{-5} M	1.0×10^{-5} M
[Iron(III)]	2.0×10^{-5}–1.6×10^{-4} M	1.6×10^{-4} M
pH	3.0–5.0	5.0
Temperature	50–90 °C	90 °C
RC_1 length	4–12 m	8 m
RC_2 length	2–8 m	6 m
Flow rates of P_1 and P_2	0.3–0.9 mL min^{-1}	0.3 mL min^{-1}

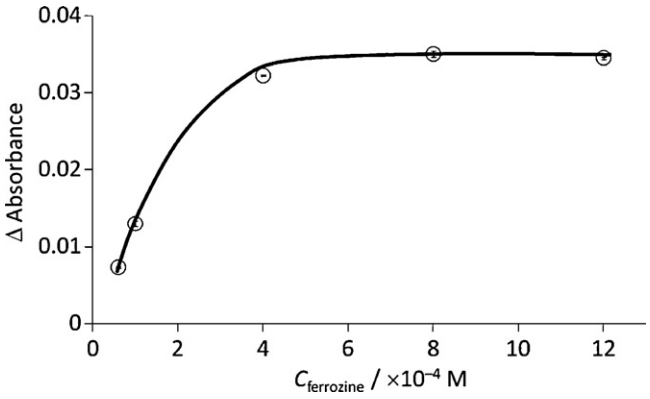

Fig. 3. Effect of ferrozine concentration on the determination of 0.25 mg L^{-1} formaldehyde. Conditions as in Fig. 1.

3.3.3. Effect of temperature

Due to the very low speed of the condensation reaction occurring in the RC_1 the heater was positioned in the FIA system. Temperature setting of the temperature control system was varied in the range of 50–90 °C. The response of HCHO monotonically increased with raising temperature. We chose therefore a temperature setting of 90 °C.

3.3.4. Effects of RC_1 and RC_2 lengths

For RC_1 in which hydroxylamine and HCHO were mixed, an 8 m-long coil (the longest coil in the examined range) was the most suitable one to help promoting the reaction. RC_2 longer than 6 m lowered the response, because the dispersion of the product occurred. An RC_2 of 6 m was therefore chosen.

3.3.5. Effect of flow rate

Flow rates of P_1 and P_2 were simultaneously varied from 0.3 to 0.9 mL min^{-1}. The highest response was obtained at a flow rate of 0.3 mL min^{-1}, and thus we chose this flow rate for each pump (note that the flow rates of 4 channels were 0.15 mL min^{-1} each).

3.4. Calibration curve

The typical system output is shown in Fig. 4. As can be seen in Fig. 4, baseline drift was observed, probably because of the

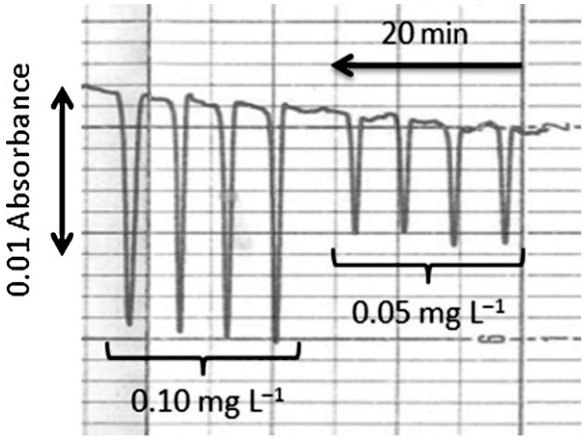

Fig. 4. Typical chart output for response to standard formaldehyde. Conditions as in Fig. 1.

Table 3
Tolerance limits of foreign metal ions and compounds on the determination of 0.25 mg L^{-1} formaldehyde.

Tolerance limit/mg L^{-1}	Added substances
50	Methyl isobutyl ketone
2	2-Butanone
0.1	Cu(II), Zn(II)
0.05	Co(II), propionaldehyde, *n*-butyraldehyde
0.02	Acetaldehyde

Table 4
Determination of formaldehyde in industrial wastewater[a].

Sample no.	Proposed method/mg L^{-1}	Acetylacetone method/mg L^{-1}
1	157 ± 3.7	155
2	8.58 ± 0.07	8.24
3	12.2 ± 0.2	11.6
4	13.4 ± 0.1	12.1
5	12.2 ± 0.2	12.6

[a] These samples were distilled and diluted with suitable ratio before measurement.

slight adsorption of the purple iron(II)–ferrozine complex on the optical window. But, practically such slight drift did not give a serious problem. The limits of detection (S/N = 3) and quantitation (S/N = 10) were 1.6 and 5.3 μg L^{-1}, and the linear range extended to 0.25 mg L^{-1}. The equation was as follows: $A = 0.140C_{HCHO} + 0.003$ with a correction coefficient of 0.994, where A is Δ absorbance and C_{HCHO} is the concentration of HCHO in mg L^{-1}. The RSD values were 0.42 and 0.36%, respectively ($n = 4$ each) for the responses at 0.05 and 0.25 mg L^{-1} standards. The sampling rate (without a distillation procedure shown below) was 12 samples h^{-1}.

3.5. Interferences

The effects of some substances that can coexist with HCHO in industrial wastewater samples were studied. For the determination of 0.25 mg L^{-1} HCHO, other aldehydes and the acetone family and some metal ions were mixed. The results are shown in Table 3. The tested aldehydes gave serious interference. Therefore we analyzed industrial wastewater after distillation [17] (see the next section).

3.6. Application to industrial wastewater

Five distilled industrial wastewater samples were analyzed by the present method and batchwise acetylacetone method [17]. The results are shown in Table 4. A paired *t*-test with 4 degrees of freedom was performed on the data obtained. The experimental *t*-value between the proposed and acetylacetone methods was 1.869. Statistical analysis revealed that the critical *t*-value for 4 degrees of freedom at the 95% confidence interval (2.776) was significantly higher than the above-mentioned experimental *t*-value. This indicates that there is no significant difference between the two methods.

4. Conclusion

We have proposed here an FI method for the spectrophotometric determination of HCHO in industrial wastewater. It was based on the condensation of HCHO with hydroxylamine and the subsequent reduction reaction of iron(III)–ferrozine complex with the residual hydroxylamine to form a purple iron(II)–ferrozine complex. The application data we obtained can support the utility of this method for being adapted as wastewater controls. The sensitivity of the present method (LOD = 1.6 μg L^{-1}) is expected to be applicable to not only wastewater analysis but also natural water analysis.

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