

# On-line collection/concentration of trace amounts of formaldehyde in air with chromatomembrane cell and its sensitive determination by flow injection technique coupled with spectrophotometric and fluorometric detection

Piyanete Sritharathikhun, Mitsuko Oshima, Shoji Motomizu\*

*Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan*

Received 19 April 2005; received in revised form 19 April 2005; accepted 19 April 2005

Available online 3 June 2005

## Abstract

A simple, rapid and highly sensitive method for the determination of trace amounts of formaldehyde in air by using flow injection analysis (FIA) system coupled with a three-hole chromatomembrane cell (CMC) was investigated by using a spectrophotometer and a fluorometer. The CMC was applied to on-line collection/concentration of trace amounts of formaldehyde in air into water as an absorbing solution; formaldehyde in the air was found to be quantitatively transferred into the absorbing solution in CMC. The solution, containing absorbed formaldehyde, was introduced into the carrier stream of the FIA system. The amount of formaldehyde in an absorbing solution was measured spectrophotometrically and fluorometrically after the reaction with a mixed reagent of acetylacetone and ammonium acetate at pH 5.6–5.8. The amount of formaldehyde in the absorbing solution, measured by the proposed system, could be converted to the concentration of formaldehyde in the air sample. A calibration graph prepared by a series of standard formaldehyde aqueous solutions was adopted. The formaldehyde in indoor air, determined as exemplified by the proposed spectrophotometric FIA, was found to be  $5.14 \pm 0.08$  ppbv for 20 ml of the air sample at the air flow rate of  $6 \text{ ml min}^{-1}$ , and the relative standard deviation (R.S.D.) was 1.56%. The limit of detections (LODs) of HCHO in an absorbing solution was  $2 \times 10^{-8} \text{ M}$  (0.6 ppb) and  $8 \times 10^{-9} \text{ M}$  (0.2 ppb), respectively, by the spectrophotometric and the fluorometric FIA, and the LODs of HCHO in air sample of 40 ml were 0.05 and 0.03 ppbv, respectively. The interferences from foreign species were examined; tolerable concentrations of other aldehydes were more than 50-fold of formaldehyde ( $1 \times 10^{-6} \text{ M}$ ).

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Spectrophotometry; Fluorometry; Air sample; Flow injection; Formaldehyde; Chromatomembrane cell; Acetylacetone

## 1. Introduction

Formaldehyde (HCHO) is considered to be a strong irritant and potential sensitizer. Inhalation of a large amount of HCHO can cause severe irritation of the upper respiratory tract and even death. Data from human exposures indicate that the exposure to high concentrations of HCHO gas may lead to pulmonary edema. Even HCHO gas present in workrooms at concentrations of 1–11 ppm can cause

eye, nose, and throat irritation. At high concentrations, formaldehyde causes headache and itchiness of the skin. Formaldehyde concentration levels in domestic air vary from ambient level (1–25 ppbv) to as high as 4 ppm in newly constructed houses [1]. Since, the regulated value for formaldehyde is  $100 \mu\text{g m}^{-3}$  (0.08 ppmv) [2]. Apart from the fact that formaldehyde is a potential carcinogenic chemical, it has recently become a matter of concern due to rising cases of sick-house syndrome, and is sometimes a very serious problem in Japan. Therefore, a rapid and sensitive method, which is applicable to air samples at low levels under a variety of environmental conditions, is required.

\* Corresponding author. Tel.: +81 862 51 7846; fax: +81 862 51 7846.  
E-mail address: [motomizu@cc.okayama-u.ac.jp](mailto:motomizu@cc.okayama-u.ac.jp) (S. Motomizu).

A large number of methods for the determination of HCHO in aqueous solutions have been developed so far. One of the most frequently used method for the determination of HCHO is HPLC coupled with the derivatization reaction using 2,4-dinitrophenylhydrazine (DNPH) followed by the measurement of the corresponding hydrazones [3–5]. HPLC procedures, however, require long analysis times and are less sensitive for the analysis of air sample. In addition, DNPH can react with most of aldehydes and ketones. Other methods, such as gas chromatography [6–8], potentiometry [9], biosensors [10], voltammetry [11,12], piezoelectric methods [13,14], solid phase microextraction (SPME) in conjugation with isotope dilution mass spectrometry (ID-MS) [15], fluorometry [16,17] and spectrophotometry [18–27], have also been reported for the determination of HCHO. Of these, a so-called Hantzsch reaction, which involves the cyclization of amine, aldehyde and  $\beta$ -diketone to form a dihydropyridine derivative, has often been used for spectrophotometric detection of HCHO in aqueous solutions. Nash [28] introduced a colorimetric method into analytical chemistry for HCHO, which was based on the Hantzsch reaction of HCHO with acetylacetone in the presence of ammonia. Later, Belman [29] found that without any other changes, a highly sensitive measurement could be made by fluorometry, instead of spectrophotometry.

A number of flow injection (FI) methods have been developed for the determination of HCHO in aqueous solutions. Gámiz-Gracia et al. [30] proposed FI spectrophotometric method coupled with pervaporation unit, where HCHO was taken up into an acidic stream of pararosaniline and spectrophotometrically monitored at 578 nm. Aiming at developing sensitive methods, fluorometric FI methods have been studied with 4-amino-3-penten-2-one [31], 1,3-cyclohexanedione [32], 5,5-dimethylcyclohexane-1,3-dione (dimedone) [33] and acridine yellow-bromate [34]. Li et al. [35] developed a FI chemiluminescence method with a bromate–rhodamine 6G system, which showed a detection limit of  $0.3 \mu\text{g l}^{-1}$  (0.3 ppb). A different FI system with immobilized formaldehyde dehydrogenase after off-line solid phase extraction for the determination of HCHO at low levels has also been reported [36]. Of these methods the most sensitive one is the fluorometry with 1,3-cyclohexanedione: limit of detection (LOD) is about  $0.2 \mu\text{g l}^{-1}$  (0.2 ppb) in an aqueous solution.

Several kinds of collection methods for gaseous analytes have been developed for the determination of HCHO. Several diffusive sampling devices have been reported with absorbents, such as 2,4-dinitrophenylhydrazine-coated silica gel [37], *N*-methyl-4-hydrazino-7-nitrobenzofurazan (MNBDH) [38], 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) coated on glass fibre filter [39]. A coil type denuder was also developed for the collection of HCHO in air [40–42]. Dasgupta and co-workers [43–47] and Toda [48] developed several kinds of gas diffusion scrubbers with a membrane tube and porous tubes for the collection of gaseous analytes. Diffusive sampling devices including denuders and

scrubbers have sometimes succeeded in the collection of gaseous analytes, followed by the detection with FI systems. In such devices, however, the efficiency of the collection of analytes in air into absorbing solutions is about 5–40%; therefore, air standards of the analytes are always necessary.

A cryotrapping sampling technique using glass traps has already been developed for monitoring carbonyl compounds followed by derivatization of DNPH and subsequent analysis by HPLC [49]. Mathews and Howell [1] used 13X molecular sieve as a sorbent medium for HCHO monitoring. In this method, HCHO-exposed sieve samples can be stored in a sealed container for approximately one month with less than 10% HCHO degradation. Another sampling method based on the derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA), which was absorbed onto poly(dimethylsiloxane)/divinylbenzene solid phase microextraction fibers, has been reported by Martos and Pawliszyn [50].

The use of hanging drops coupled with optical fiber chemical sensors for the determination of HCHO with the LOD of 2 ppbv have been developed [51–53]. Li et al. [45] proposed a thermostated diffusion scrubber for sampling atmospheric formaldehyde coupled with a GaN-based light-emitting diode (LED) as the excitation source in a miniature flowthrough fluorescence detector based on a transversely illuminated liquid-core waveguide, which provided a fully automated instrument. By using these collection methods, the sensitivity is not enough for the determination of sub-ppbv in HCHO in air, and the air standards for the analytes are requisite to the preparation of a calibration graph.

The chromatomembrane cell (CMC), which is proposed for the transfer of analytes from one phase to another, has been proved to be a very useful device for sample pretreatment, as evidenced by on-line collection/concentration using liquid–liquid extraction [54,55], continuous gas–liquid extraction [48,49], and the transfer of gaseous substances into liquids [56–63]. Zhang et al. [62] used a CMC for collecting HCHO in air and determined by a batchwise adsorptive polarographic determination: the volume of the CMC used was too large ( $25 \text{ mm} \times 25 \text{ mm} \times 50 \text{ mm}$ ) to be used for on-line collection. Recently, Motomizu and co-workers successfully employed FI system coupled with a small-volume cylindrical CMC ( $\phi = 12 \text{ mm}$ ,  $h = 14 \text{ mm}$ ) for the determination of nitrogen dioxide [59–61] and sulfur dioxide [63] in the atmosphere. One of the advantages of the collection/concentration with the small-volume CMC is the good efficiency of the mass transfer from air to small-volume of absorbing solutions: the efficiencies were about 98% or more [59,63]. Such results indicate that calibration graphs prepared by using aqueous standard solutions can be conveniently used for the analysis of air.

In this work, a spectrophotometric and fluorometric FI system coupled with the three-hole CMC for the determination of HCHO in air samples were investigated and applied to the determination of trace amounts of HCHO in air. As a

detection reaction, the acetylacetone reaction, which has scarcely applied to flow injection method, was selected because of possible detection by both spectrophotometric and fluorometric methods, relatively high sensitivity, relatively moderate reaction under the conditions of low reaction temperature, short reaction time, less expensive and versatile reagents.

## 2. Experimental

### 2.1. Apparatus

A schematic diagram of a flow injection analysis (FIA) system coupled with the three-hole CMC is shown in Fig. 1. A double-plunger pump (Sanuki Kogyo, SRX3400T, Japan), P1, was used for propelling a reagent (RS) and a carrier (CS) solution, and carrying the HCHO absorbed solutions in the CMC into a carrier stream. A peristaltic pump (Nippon Rikagaku Kikai, PF-7, Japan), P2, was used for propelling the absorbing solution into the CMC. A syringe-type pump (KD Scientific, 210P, USA), P3, was used for introducing adequate volumes of air samples into the CMC at a given flow rate. Two six-way valves (Sanuki Kogyo), V1 and V2, were used for introducing standard HCHO aqueous solutions and for introducing the absorbing solution into the CMC or the carrier solution through the CMC into the carrier stream of FIA system. The 0.5 mm i.d. PTFE tubing was used for flow lines except for the back-pressure coil (0.25 mm i.d. tubing). The absorbance was measured at 412 nm by a visible detector

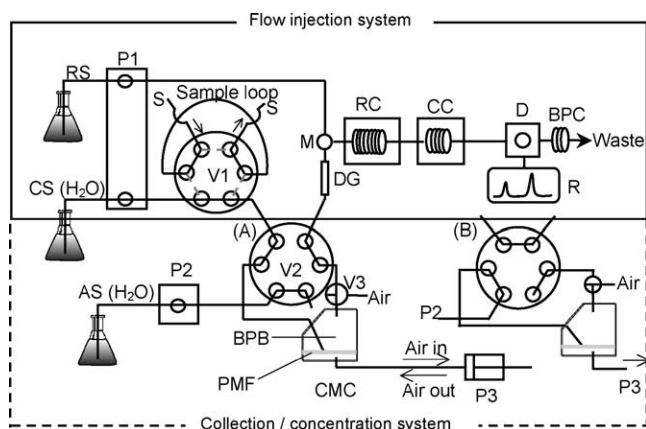


Fig. 1. Schematic flow injection system coupled with a collection/concentration system for formaldehyde determination. RS, reagent solution (0.03 M acetylacetone in 2 M ammonium acetate at pH 5.6–5.8); CS and AS, carrier and absorbing solutions (ultrapure water); P1, double-plunger pump (each flow rate,  $0.4 \text{ ml min}^{-1}$ ); P2, peristaltic pump (flow rate,  $0.5 \text{ ml min}^{-1}$ ); P3, syringe-type pump (flow rate,  $5 \text{ ml min}^{-1}$ ); V1 and V2, six-way valves; V3, three-way valve; S, sample; M, mixing joint; DG, degassing unit; RC, reaction coil ( $0.5 \text{ mm i.d.} \times 500 \text{ cm}$ ); CC, cooling coil ( $0.5 \text{ mm i.d.} \times 200 \text{ cm}$ ); D, detector (spectrophotometer and/or fluorometer); R, recording system (integrator or PC); BPC, back-pressure coil ( $0.25 \text{ mm i.d.} \times 30 \text{ cm}$ ); CMC, chromatomembrane cell; BPB, biporous PTFE block ( $\phi = 12 \text{ mm}$ ,  $h = 14 \text{ mm}$ ); PMF, porous membrane filter. (A) Absorbing solution is introduced to the FIA system; (B) air is sampled.

(Soma, S-3250, Japan) with a micro flow-through cell (volume  $8 \mu\text{l}$ ; path length  $10 \text{ mm}$ ) and by a fluorescence detector (Shimadzu, RF-10A XL, Japan) with a micro flow-through cell ( $8 \mu\text{l}$ ). The peak area and peak height were recorded with an integrator (Hitachi, D-2500, Japan) or with a notebook computer system (FIA monitors; FIA Instruments, Japan). The CMC was assembled with a biporous PTFE block (BPB) and a piece of hydrophobic PTFE membrane filter (Toyo Roshi, Advantec T020A090C, pore size  $0.2 \mu\text{m}$ , Japan), as previously described [59–61,63]. All experiments were performed in a controlled-temperature room ( $25.0 \pm 0.1^\circ\text{C}$ ).

### 2.2. Reagents

All chemicals used in this work were of analytical reagent grade, and the water purified with a Milli-Q Labo (Millipore) was used for the preparation of all solutions. The reagent solution (RS) was prepared by mixing 1 M acetylacetone stock solution and 3.0 M ammonium acetate stock solution, followed by the addition of acetic acid for the purpose of adjusting concentrations and pH. An acetylacetone stock solution was prepared by diluting 5.0 ml of acetylacetone (Wako Pure Chemicals, Osaka, assay minimum 99.0%) with the purified water to give a 50 ml solution. An ammonium acetate stock solution was prepared by dissolving 57.8 g of ammonium acetate (Wako Pure Chemicals) in the purified water and diluting it to 250 ml with the purified water.

A 0.1 M standard stock solution of formaldehyde was prepared by diluting 0.8 ml of 36.0–38.0% HCHO solution (Wako Pure Chemicals) to 100 ml with the purified water; the accurate concentration of this solution was determined by an iodometric method. The working standards were daily prepared by accurate dilution of the standard stock solution.

### 2.3. Procedures for the determination of formaldehyde

#### 2.3.1. Flow injection procedure for the determination of formaldehyde in aqueous solutions

A diagram of the flow injection system used in this work is shown in Fig. 1. Pump P1 was used for propelling carrier and reagent solutions. In the proposed method, the flow rate of the carrier and of the reagent solution was set at  $0.4 \text{ ml min}^{-1}$ . A six-way valve with a sample loop ( $300 \mu\text{l}$ ) was used to introduce the working standards of HCHO into the carrier stream for the preparation of a calibration graph. Absorbance or fluorescence changes of the reaction product were measured by the visible detector (412 nm) and the fluorescence detector: excitation and emission wavelength were 420 and 505 nm, respectively. The flow signals were recorded with an integrator and a notebook-type computer: peak height and peak area were used for the preparation of the calibration graph.

#### 2.3.2. Batchwise collection/concentration method for the determination of HCHO in air sample

Formaldehyde in air samples is desired to be absorbed quantitatively into absorbing solutions, and the HCHO

concentrations in the absorbing solutions had better be determined as accurately as possible by a reproducible method in order to obtain reliable data for HCHO concentrations in air samples. Accurate concentrations of the HCHO in the absorbing solutions were measured by the FIA system (Fig. 1).

The batchwise collection of HCHO from air samples into an absorbing solution was investigated as follows. Accurate volumes of 50 ml plastic syringes as an air sampling vessel were measured by weighting the maximum volume of water filled in the syringes. The volumes of the syringes were found to be  $71.92 \pm 0.43$  ml when the piston stopped at the top of the syringes, which means that the volumes of the syringes are very reproducible and the syringes can be used as an air sampling vessel for sampling air. Three millilitres of the absorbing solution (the purified water) was transferred into the plastic syringes using a piston-type pipette (Eppendorf, Germany), and the syringes were immediately capped in order to avoid the contamination of HCHO from the surrounding environment. The air sampling vessels (syringes) were then carried to sampling sites, where air samples were introduced into the vessels and then the vessels were capped again. The vessels filled with air were brought back to an experimental laboratory for the measurement of HCHO concentrations in the absorbing solutions in the sampling vessels by FIA. The air sampling vessels were shaken vigorously by hand for a certain periods of times (4 min). After shaking, the absorbing solutions in the vessels were introduced into the FIA system using a six-way injection valve (300  $\mu$ l) for HCHO measurement. The concentrations of HCHO in air samples can be calculated from the concentration of HCHO in the absorbing solution, the collection efficiency and the concentration factor of HCHO. In this experiment with the 50-ml syringe, the actual concentration factor was  $V_{\text{air}}/V_1 = 68.92/3.00 = 22.97$ , where  $V_{\text{air}}$  and  $V_1$  represent the volume of the air sample ( $68.92 = 71.92 - 3.00$  ml) and the absorbing solution (3.00 ml), respectively.

#### 2.3.3. On-line collection/concentration method for the determination of HCHO in air sample

As shown in Fig. 1, the FIA system coupling the collection/concentration system with the three-hole CMC was assembled for HCHO determination. To start the analysis, the pump P2 was started and the absorbing solution was propelled into the CMC at the flow rate of  $0.5 \text{ ml min}^{-1}$ . After filling up the CMC, the pump P2 was stopped, and the pump P3 was started to introduce air sample into the CMC at the flow rate of  $6 \text{ ml min}^{-1}$ . While the air sample was introduced, the analyte was being continuously transferred from air to the absorbing solution in the CMC, where HCHO was being collected and concentrated (see Fig. 1(B)). Then, the absorbing solution in the CMC was introduced into the carrier stream by turning the six-way valve, V2, to an injection position (see Fig. 1(A)). The absorbing solution was mixed with the reagent solutions, and flowed into the reaction coil (RC), which was wound round an aluminium cylinder

block controlled at  $60^\circ\text{C}$ . At the downstream of the reaction coil, the solution was cooled down to a room temperature with a water bath prior to the detection of absorbance or the detection of fluorescence. After the measurement, the valve V2 was turned to the load position, and P3 was restarted in the reverse position to introduce the HCHO-free air, which was kept in the syringe of the pump, into the CMC at the flow rate of  $15 \text{ ml min}^{-1}$ . The CMC was refreshed by this procedure and could be used repeatedly without deterioration. The measurement time necessary for one sample was about 7 min, when 20 ml of air sample was used at the sampling flow rate of  $6 \text{ ml min}^{-1}$ .

### 3. Results and discussion

#### 3.1. Optimisation of experimental variables for flow injection method

The acetylacetone method has scarcely applied to flow injection methods though it has several possible advantages. In this work, the optimal conditions were examined with respect of improving the sensitivity of HCHO determination under the moderate conditions.

The optimisation experiments were performed by the FIA manifold with spectrophotometric detection in Fig. 1. In the reaction of HCHO with the reagents, reaction temperature and reaction time are very important for the reaction efficiency of HCHO. The effect of temperature on the absorbance was examined by varying temperature from 25 to  $70^\circ\text{C}$  using the heating system. The absorbance increased with an increase in temperature until  $55^\circ\text{C}$ , beyond which absorbance remained constant. Thus, a temperature of  $60^\circ\text{C}$  was chosen for further studies.

The acetylacetone concentration was examined in the range of 0.001–0.08 M, while ammonium acetate concentration and pH were kept constant at 2 M and 5.8, respectively. The absorbance increased with an increase in acetylacetone concentration till 0.02 M, beyond which absorbance kept identical. Thus, acetylacetone concentration of 0.03 M was chosen.

The effect of ammonium acetate concentration was examined in the range of 0.25–3.0 M, while the acetylacetone concentration and pH were kept constant at 0.03 M and 5.8, respectively. The absorbance increased with an increase in ammonium acetate concentration. However, at higher concentrations, the increase in absorbance was accompanied by an increase in noise levels. In order to compromise between two effects, the concentration of 2 M was chosen.

The effect of pH of the reagent solution was varied in the range of 4.5–7.8 using acetic acid and ammonia solution. The results obtained are shown in Fig. 2(a). In the pH range of 5.2–6.8, the peak intensities were almost constant, while below pH 5.2 and above pH 6.8, the peak intensities decreased drastically. Based on these results, the pH range of 5.6–5.8 was chosen for further studies.



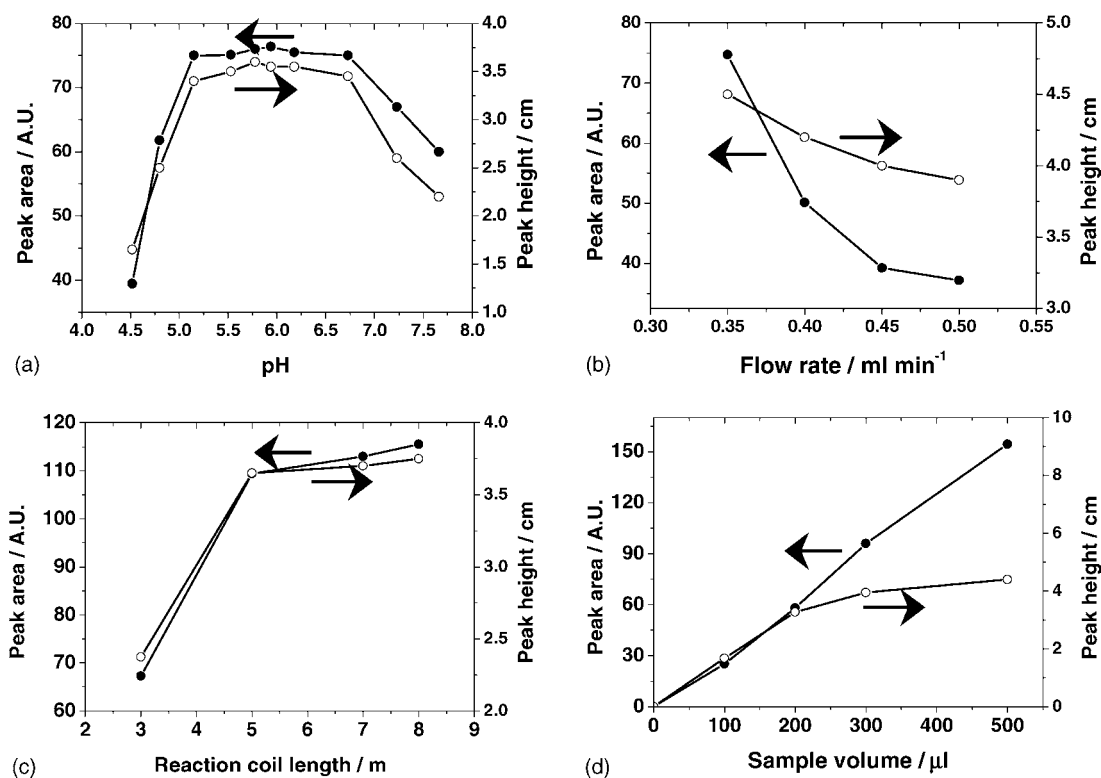


Fig. 2. Optimisation of experimental conditions on the absorbance. Sample,  $1 \times 10^{-6}$  M formaldehyde, 300  $\mu$ l. (a) pH; (b) flow rate of FI system; (c) reaction coil length; (d) sample volume.

The effect of flow rate of the carrier and the reagent solutions in the range of 0.35–0.50 ml min<sup>-1</sup> was investigated under the optimum reagent composition. The results obtained (Fig. 2(b)) indicate that the peak intensity decreases with increasing flow rate. In order to compromise sensitivity and analysis time, each flow rate of 0.4 ml min<sup>-1</sup> was adopted for further studies.

The effect of reaction coil length was also examined. The reaction coil length studied was of 3–8 m. As depicted by Fig. 2(c), it was found that the absorbance increased with an increase in reaction coil length until 5 m, after which signal increases were gradual. Therefore, a 5 m coil was chosen for further studies.

The sample injection volumes of 100, 200, 300 and 500  $\mu$ l were tested under the optimum conditions described above. The results obtained (Fig. 2(d)) suggested that larger volumes were preferable to obtain the higher peak intensity and the volume beyond 300  $\mu$ l gave almost identical peak height. A sample volume of 300  $\mu$ l was used for rapid analyte measurement.

The optimisation of the experimental conditions for fluorometric detection was also studied. It was found that the optimum conditions were the same as in the spectrophotometric detection.

### 3.2. Interferences of coexisting substances

The investigation of possible interferences was conducted with regard to possible chemical interferences and the

problems of selectivity. The results obtained are summarized in Table 1, where the tolerable concentration was defined as the concentration of foreign species causing less than  $\pm 5\%$  relative error. The results revealed no serious interference from most aldehyde, cations and anions, except Fe<sup>2+</sup> and Fe<sup>3+</sup>, both of which could be masked by EDTA. In most of the spectrophotometric and fluorometric methods, acetaldehyde can cause interference with the determination of formaldehyde. In the proposed system, however, the interference of acetaldehyde is much less compared with other methods. This is because acetaldehyde, as well as other aldehydes except for formaldehyde, can react with acetylacetone and ammonia under the conditions of higher temperature and longer time. By selecting the moderate conditions for the reaction of HCHO, the selectivity was

Table 1  
Tolerable concentration of foreign species in the determination of  $1 \times 10^{-6}$  M HCHO

Species	Concentration limit (M)
Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Li <sup>+</sup> , Ca <sup>2+</sup> , V(V), Mo(VI), Cl <sup>-</sup> , Br <sup>-</sup> , methanol, ethanol, EDTA	$1 \times 10^{-2}$
Pb <sup>2+</sup> , Al <sup>3+</sup> , H <sub>2</sub> O <sub>2</sub> , propionaldehyde, benzaldehyde	$1 \times 10^{-4}$
NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> , acetone, NH <sub>4</sub> <sup>+</sup> , Cd <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Mn <sup>2+</sup> , Cu <sup>2+</sup> , Co <sup>2+</sup> , acetaldehyde	$5 \times 10^{-5}$
SO <sub>3</sub> <sup>2-</sup>	$1 \times 10^{-5}$
Fe <sup>2+</sup> , Fe <sup>3+</sup>	$2 \times 10^{-6}$

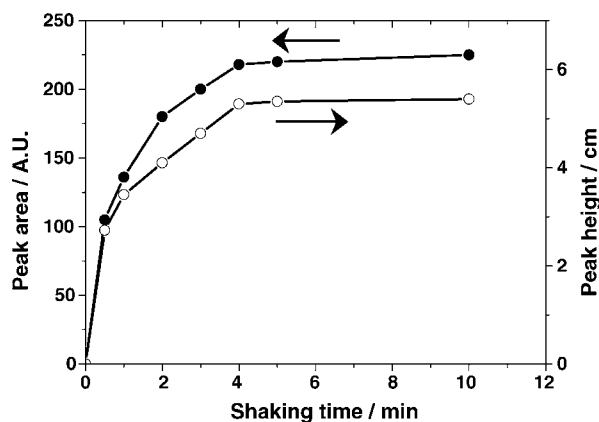


Fig. 3. Effect of shaking time on absorbance of formaldehyde in the absorbing solution. Air sample, sampled at our laboratory on December 11, 2003; absorbing solution, Milli-Q water.

highly improved in the present study with FIA system [28–29].

### 3.3. Optimisation of experimental variables of batchwise collection/concentration method

The batchwise collection method was necessary for examining the collection efficiency of HCHO in air by on-line system, as well as for determining HCHO in air by FIA measurement coupled with the batchwise method. The effect of shaking time on the absorption efficiency of HCHO from air sample into purified water was examined from 1 to 6 min, using 3.00 ml of the purified water as an absorbing solution in a 50 ml plastic syringe volume:  $71.92 \pm 0.43$  ml. The result obtained (Fig. 3) shows that the peak height became almost constant when the shaking time was longer than 3 min, which suggests that HCHO from the air sample was completely transferred to the absorbing solution after shaking more than 3 min. In further experiments, 4 min was selected.

The quantitative absorption efficiency of HCHO into purified water was examined by three consecutive collections, each using 3 ml of purified water in the 50 ml plastic syringe for the same air sample. In the first collection, the collection efficiency was more than 99%, while in the second and the third collection, the efficiency was less than 0.5%. The signals obtained in the second and third procedures were nearly at the background level. These results suggest that HCHO in the 50 ml air sample could be quantitatively absorbed in 3 ml of water in a single collection.

### 3.4. Optimisation of on-line collection/concentration of formaldehyde in air

The effect of sampling flow rate on on-line collection/concentration efficiency by using the chromatomembrane cell was studied. The effect of sampling flow rate of air sample on the peak area and peak height was examined in the range of  $3\text{--}10\text{ ml min}^{-1}$ , using 20 ml of air sample, which was

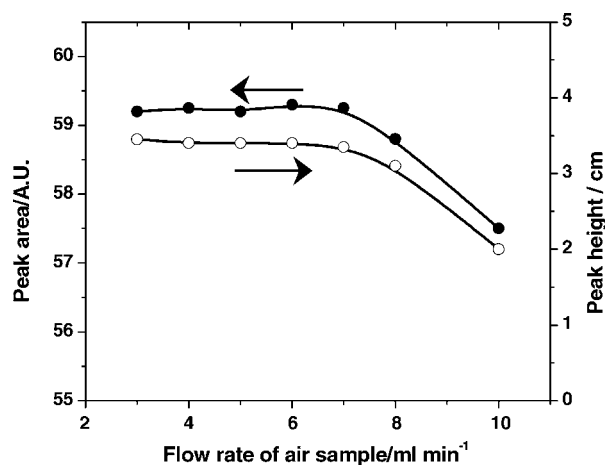


Fig. 4. Effect of sampling flow rate of air sample on absorbance. Air sample, 20 ml.

collected in our laboratory (indoor air). The results obtained are shown in Fig. 4. When the flow rate of the air sample exceeded  $7\text{ ml min}^{-1}$ , the peak area and peak height decreased abruptly. At the flow rate of air sample  $3\text{--}7\text{ ml min}^{-1}$ , the absorbances obtained were almost constant;  $6\text{ ml min}^{-1}$  was therefore chosen for further studies.

The effect of air sample volume on the peak area and peak height was examined in the range of 5–30 ml, keeping the flow rate of air sample at  $6\text{ ml min}^{-1}$ . Fig. 5 shows the results obtained. The peak area increased linearly with an increase in the sample volume up to 40 ml, whereas the peak height increased linearly with an increase in the sample volume until 20 ml, after which it increased gradually. Such phenomena support the principle of collection with CMC described in the previous works [59–61]; i.e., the analyte absorbed into the absorbing solution is related to the analyte concentration of the gaseous sample, and the absorbed zone changes according to the volume of the gaseous sample, which leads to a constant peak height. In this work, 20 ml of the sample volume was chosen because of the sufficient sensitivity for the determination of HCHO in air.

### 3.5. Preparation of calibration graph

In the present FIA method, the peak height was not suitable for making calibration graphs, because there was no linear relationship between the HCHO concentration in air sample and the peak height. Wei and co-workers [59–61] showed a good relationship between the peak area and the mass of an analyte in the air sample passed through the CMC according to the law of conservation of mass, when the absorption efficiency was 100%. The collection of HCHO in the air sample into water was examined by both the batchwise collection/FIA method and the on-line collection/FIA method, where the standard aqueous solutions of HCHO were used for preparing the calibration graph at the concentration range of  $1.5\text{--}15 \times 10^{-7}\text{ M}$ . The HCHO concentrations were changed into mole unit and plotted against

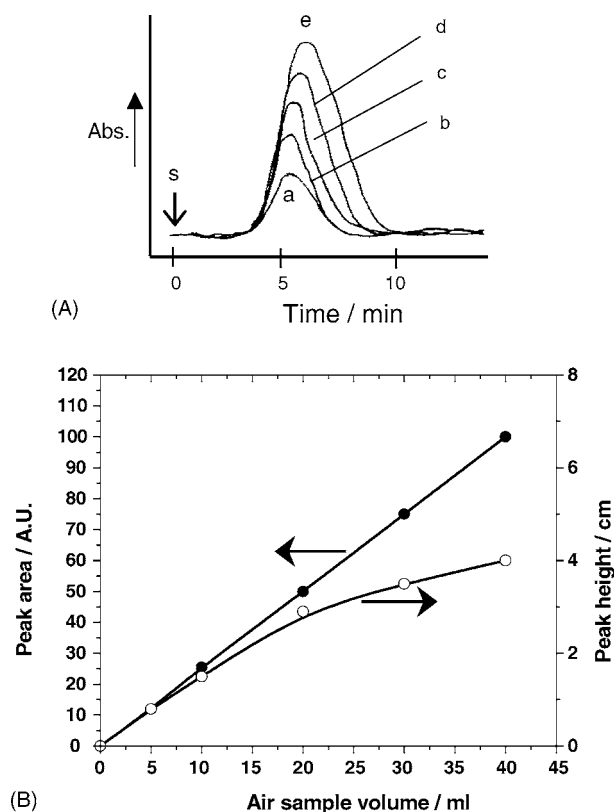


Fig. 5. Effect of air sample volume on absorbance. Flow rate of air sample:  $6 \text{ ml min}^{-1}$ ; volume of air samples a, b, c, d and e are 5, 10, 20, 30 and 40 ml, respectively; S: sample injection. (A) Signal profiles; (B) air sample volume against peak area and peak height.

peak area to yield a linear calibration graph. The equation of the calibration graph was expressed as  $A = 1.62Q + 0.44$  and  $A = 1.95Q + 0.22$  for the spectrophotometric and the fluorometric detection, respectively, where  $A$  was peak area and  $Q$  was total quantity of HCHO in  $10^{-11} \text{ mol}$ . The correlation coefficients of both systems were 0.9989. By using the calibration graph for the spectrophotometry, the concentrations of HCHO in air were determined by using the batchwise collection and the on-line collection methods. The results show that the both concentrations were in good agreement with each other as is shown in Table 2, which means that HCHO in air can be almost completely collected in water with CMC and therefore the aqueous standard solution of HCHO can be used for the preparation of a calibration graph. The possibility of using the aqueous standard solution of HCHO for the preparation of a calibration graph is very important and useful advantage of the proposed on-line system with CMC over other collection systems, such as diffusion scrubbers and denuders, which need standard gas samples.

### 3.6. Reproducibility test and limit of detection (LOD)

The reproducibility of the proposed method was examined for real air samples, where the samples used for the HCHO determination were 20 ml and the sampling flow rate

Table 2

Analytical results for HCHO determination in air samples by spectrophotometric FI

Sample <sup>a</sup>	HCHO (ppbv)	
	Batchwise collection	On-line collection
Outdoor 1 <sup>a</sup>	$3.85 \pm 0.08$	$3.53 \pm 0.23$
Outdoor 2 <sup>a</sup>	$5.93 \pm 0.08$	$6.05 \pm 0.10$
Outdoor 3 <sup>a</sup>	$5.74 \pm 0.12$	$5.60 \pm 0.14$
Indoor 1 <sup>b</sup>	$7.21 \pm 0.07$	$7.55 \pm 0.16$
Indoor 2 <sup>c</sup>	ND	$5.14 \pm 0.08$
Indoor 3 <sup>d</sup>	ND	$3.58 \pm 0.10$
Indoor 4 <sup>e</sup>	ND	$4.88 \pm 0.15$

ND: not done the measurements.

<sup>a</sup> Samples: 20 ml, sampled at the campus of Okayama University on February 11, 2004.

<sup>b</sup> Sample: 20 ml, sampled at Anal. Chem. Lab of Okayama University on February 11, 2004.

<sup>c</sup> Sample: 20 ml, sampled at Anal. Chem. Lab of Okayama University on February 13, 2004.

<sup>d</sup> Sample: 20 ml, sampled at Anal. Chem. Lab of Okayama University on February 14, 2004.

<sup>e</sup> Sample: 20 ml, sampled at Anal. Chem. Lab of Okayama University on February 15, 2004.

was  $6 \text{ ml min}^{-1}$ . The average concentration of HCHO in the air sample was  $5.14 \pm 0.08 \text{ ppbv}$  (mean  $\pm \sigma$ ) with the relative standard deviation (R.S.D.) of 1.56%. The LODs for the determination of HCHO in the air sample, which was defined as the concentration corresponding to three times of standard deviation (S.D.) of the air sample (HCHO 1.2 ppbv) by using 40 ml of the diluted air sample, were 0.05 and 0.03 ppbv, by the spectrophotometric and fluorometric/FIA, respectively. In Fig. 6, the flow signals obtained by the fluorometric FIA were shown. This result indicates that the reproducible peaks can be obtained even for HCHO at low concentrations.

### 3.7. Application of the proposed method to real samples

The proposed method was applied to the determination of HCHO in real air samples, using 20 ml of air with the flow

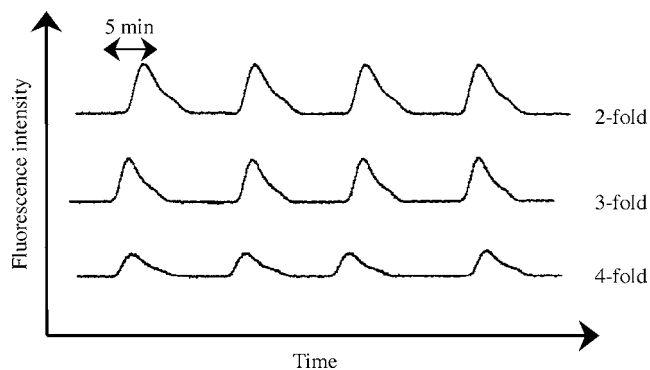


Fig. 6. Reproducibility of peak shape obtained using diluted air samples by fluorometric/FIA. Sample: a real air was diluted to two, three and four-fold with  $\text{N}_2$  gas, 40 ml of which was analyzed. Samples: air was collected in our laboratory of Okayama University on May 1, 2004; HCHO concentration, 4.80 ppbv. The regression equation:  $A = 2.16 Q + 0.06$ , where  $A$  = peak area,  $Q$  = total quantity of HCHO in diluted air.

Table 3

The comparison of the performance between on-line CMC and batchwise collection methods

Features	Collection method	
	On-line CMC	Batchwise
Sensitivities	Very good	Good
Automation	Allowed	Not allowed
Total analysis time	Short	Long
Precision	Very good	Good
Sample volume	Small	Large

rate of  $6 \text{ ml min}^{-1}$ . The results were compared with those obtained by the batchwise collection/FIA method as shown in Table 2. The analytical results obtained by the on-line collection/FIA system were in good agreement with those obtained by the batchwise collection/FIA method. Moreover, it can be seen that the HCHO concentration in our indoor air samples lower than the regulated value (0.08 ppmv) [2].

#### 4. Conclusion

In the present work, a simple, rapid and sensitive FI system for the determination of HCHO in air was developed, where the FI system was coupled with a three-hole chromatomembrane cell (CMC). The formaldehyde aqueous solutions could be used as the standard solutions for preparing the calibration graph, which was very useful and convenient for the practical analysis because standard HCHO gas was not required. By using the moderate reaction conditions, the selectivity of HCHO detection was improved, and the interference from acetaldehyde, as well as other aldehydes, was much decreased. The LODs estimated by using 40 ml of diluted air sample were 0.05 and 0.03 ppbv, by the spectrophotometric and fluorometric/FIA, respectively. The advantages of the on-line CMC and batchwise collection are shown in Table 3.

#### Acknowledgements

This work was supported partially by the Grant-in-Aid for Scientific Research (B) (2) (No. 16350044) from Japan Society for the Promotion of Science (JSPS), and partly by the Venture Business Laboratory of Okayama University.

#### References

- [1] T.G. Matthews, T.C. Howell, *Anal. Chem.* 54 (1982) 1495.
- [2] Report of Mini Association on Chemical Substances by the Ministry of Health of Japan, 1997.
- [3] D. Grosjean, K. Fung, *Anal. Chem.* 54 (1982) 1221.
- [4] K. Takami, K. Kuwata, A. Sugimae, A. Nakamoto, *Anal. Chem.* 57 (1985) 243.
- [5] F. Sandner, W. Dott, J. Hollender, *Int. J. Hyg. Environ. Health* 203 (2001) 275.
- [6] C.L.P. Thomas, C.D. McGill, R. Towil, *Analyst* 122 (1997) 1471.
- [7] T. Shiraishi, Y. Soma, O. Ishitani, K. Sakamoto, *J. Environ. Monit.* 3 (2001) 654.
- [8] J.R. Hopkins, T. Still, S. Al-Haider, I.R. Fisher, A.C. Lewis, P.W. Seakins, *Atmos. Environ.* 37 (2003) 2557.
- [9] Y.I. Korpan, M.V. Gonchar, A.A. Sibirny, C. Martelet, A.V. El'skaya, T.D. Gibson, A.P. Soldatkin, *Biosens. Bioelectron.* 15 (2000) 77.
- [10] R. Katakya, M.R. Bryce, L. Goldenberg, S. Hayes, A. Nowak, *Talanta* 56 (2002) 451.
- [11] W.H. Chan, T.Y. Xie, *Anal. Chim. Acta* 349 (1997) 349.
- [12] M. Yang, X.G. Zhang, H.L. Li, *Analyst* 126 (2001) 676.
- [13] O. Fatibello-Filho, A.A. Suleiman, G.G. Guibault, *Talanta* 38 (1991) 541.
- [14] R.L. Bunde, E.J. Jarvi, J.J. Rosentreter, *Talanta* 51 (2000) 159.
- [15] R.T. Rivero, V. Topiwala, *J. Chromatogr. A* 1029 (2004) 217.
- [16] S.T. Grousi, E.E. Golia, A.N. Voulgaropoulos, A.J. Maroulis, *Fresenius J. Anal. Chem.* 358 (1997) 667.
- [17] X.-Q. Zhan, D.-H. Li, Q.-Z. Zhu, H. Zheng, J.-G. Xu, *Analyst* 125 (2000) 2330.
- [18] A.C. Rayner, C.M. Jephcott, *Anal. Chem.* 33 (1961) 627.
- [19] E. Sawicki, T.R. Hauser, S. McPherson, *Anal. Chem.* 34 (1962) 1460.
- [20] B.W. Bailey, J.M. Rankin, *Anal. Chem.* 43 (1971) 782.
- [21] R.R. Miksch, D.W. Anthon, L.Z. Fanning, C.D. Hollowell, K. Revzan, J. Glanville, *Anal. Chem.* 53 (1981) 2118.
- [22] P. Verma, V.K. Gupta, *Talanta* 30 (1983) 443.
- [23] A. Afkhami, M. Rezaei, *Microchem. J.* 63 (1999) 243.
- [24] A.A. Ensafi, S. Abassi, *Fresenius J. Anal. Chem.* 363 (1999) 376.
- [25] S.K. Goyal, *J. Environ. Monit.* 3 (2001) 666.
- [26] J.M. Bosque-Sendra, S. Pescarolo, L. Cuadros-Rodríguez, A.M. García-Campaña, E.M. Almansa-López, *Fresenius J. Anal. Chem.* 369 (2001) 715.
- [27] P. Tomčík, L. Mrafková, D. Bustin, *Microchim. Acta* 141 (2003) 69.
- [28] T. Nash, *Biochem. J.* 55 (1953) 416.
- [29] S. Belman, *Anal. Chim. Acta* 29 (1963) 120.
- [30] L. Gámiz-Gracia, M.D. Luque de Castro, *Analyst* 124 (1999) 1119.
- [31] H. Tsuchiya, S. Ohtani, K. Yamada, M. Akagiri, N. Takagi, *Analyst* 119 (1994) 1413.
- [32] Q. Fan, P.K. Dasgupta, *Anal. Chem.* 66 (1994) 551.
- [33] T. Sakai, S. Tanaka, N. Teshima, S. Yasuda, N. Ura, *Talanta* 58 (2002) 1271.
- [34] T. Pérez-Ruiz, C. Martínez-Lozana, V. Tomás, J. Fenoll, *Anal. Bioanal. Chem.* 375 (2003) 661.
- [35] B. Li, M. Liu, Z. Zhang, C. Xu, *Anal. Sci.* 19 (2003) 1643.
- [36] N. Kiba, L. Sun, S. Yokose, M.T. Kazue, T.T. Suzuki, *Anal. Chim. Acta* 378 (1999) 169.
- [37] S. Uchiyama, S. Hasagawa, *Atmos. Environ.* 33 (1999) 1999.
- [38] A. Büldt, R. Lindahl, J.-O. Levin, U. Karst, *J. Environ. Monit.* 1 (1999) 39.
- [39] W.H. Chan, S. Shuang, M.M.F. Choi, *Analyst* 126 (2001) 720.
- [40] A.L. Lazrus, K.L. Fong, J.A. Line, *Anal. Chem.* 60 (1988) 1074.
- [41] K. Riedel, R. Weller, O. Schrems, *Phys. Chem. Chem. Phys.* 1 (1999) 5523.
- [42] H.-W. Jacobi, M.M. Frey, M.A. Hutterli, R.C. Bacles, O. Schrems, N.T. Cullen, K. Steffen, C. Koehler, *Atmos. Environ.* 36 (2002) 2619.
- [43] S. Dong, P.K. Dasgupta, *Environ. Sci. Technol.* 20 (1986) 637.
- [44] P.K. Dasgupta, S. Dong, *Atmos. Environ.* 26 (1986) 565.
- [45] J. Li, P.K. Dasgupta, Z. Genfa, M.A. Hutterli, *Field Anal. Chem. Technol.* 5 (2001) 2.
- [46] K. Toda, P.K. Dasgupta, J. Li, G.A. Tarrer, G.M. Zarus, *Anal. Chem.* 73 (2001) 5716.
- [47] K. Toda, S. Ohira, T. Tanaka, T. Nishimura, P.K. Dasgupta, *Environ. Sci. Technol.* 38 (2004) 1529.
- [48] K. Toda, *Anal. Sci.* 20 (2004) 19.
- [49] A. Levart, M. Veber, *Chemophore* 44 (2001) 701.
- [50] P.A. Martos, J. Pawliszyn, *Anal. Chem.* 70 (1998) 2311.
- [51] E.A. Pereira, P.K. Dasgupta, *Int. J. Environ. Anal. Chem.* 66 (1997) 201.



- [52] A. Pretto, M.R. Milani, A.A. Cardoso, J. Environ. Monit. 2 (2002) 566.
- [53] M. Kumemura, T. Yamauchi, C. Hara, M.I.H. Helaleh, T. Korenaga, Anal. Sci. 17 (Suppl.) (2001) i453.
- [54] L.N. Moskvina, J. Simon, Talanta 41 (1994) 1765.
- [55] L.N. Moskvina, J. Simon, P. Löffler, N.V. Michailova, D.N. Nicolaeva, Talanta 43 (1996) 819.
- [56] L.N. Moskvina, O.V. Rodinkov, J. Chromatogr. A 725 (1996) 351.
- [57] P. Löffler, J. Simon, A. Katruzov, L.N. Moskvina, Fresenius J. Anal. Chem. 352 (1995) 613.
- [58] L.N. Moskvina, T.G. Nikitina, J. Anal. Chem. 54 (1999) 290.
- [59] Y. Wei, M. Oshima, J. Simon, L.N. Moskvina, S. Motomizu, Talanta 58 (2002) 1343.
- [60] Y. Wei, M. Oshima, J. Simon, S. Motomizu, Talanta 57 (2002) 355.
- [61] Y. Wei, M. Oshima, J. Simon, S. Motomizu, Anal. Sci. 17 (Suppl.) (2001) a325.
- [62] Z.-Q. Zhang, H. Zhang, G.-F. He, Talanta 57 (2002) 317.
- [63] P. Sritharathikhun, M. Oshima, Y. Wei, J. Simon, S. Motomizu, Anal. Sci. 20 (2004) 113.