On-site Analysis of Trace Amounts of Formaldehyde in Ambient Air Using Batchwise Collection/Concentration Method and Portable Flow Injection System

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Abstract

A simple and rapid method for the determination of formaldehyde (HCHO) in air was developed by using a portable flow injection analysis (FIA) system installed with a detector consisting of a light emitting diode (LED) as a light source, and a flow cell and with a heating system. The method was used for on-site measurement by coupling with a simple batchwise absorption collection method. HCHO in air was collected quantitatively on-site in a 50-ml syringe (volume: 71.92±0.43 ml) containing 3 ml of purified water as an absorbing solution, which was subsequently introduced into the carrier stream of the FIA system. The amounts of HCHO in the absorbing solution were measured at 450 nm after reaction with a mixed reagent of acetylacetone and ammonium acetate at pH 6.0 or with a fluoral P solution of 0.4 M phosphate buffer (pH 6.0). A calibration graph with standard HCHO aqueous solutions could be adopted for the determination of formaldehyde in air. The relative standard deviation (RSD) was 0.63% for $1x10^{-5}$ M (n = 12) and with the limit of detection (LOD) was $2.7x10^{-8}$ M (0.8 ppb) in aqueous solution (S/N =3), which corresponds to 35 pptv of HCHO in air. The proposed method was successfully applied to air samples

Keywords Formaldehyde, Air sample, Spectrophotometry, Flow injection, Batchwise collection

1. Introduction

Formaldehyde (HCHO) is considered to be an important organic compound in industrial synthesis and is known to be an indoor air contaminant. The main sources for the HCHO pollution in air include painting, coating material and cigarette smoking. 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 high concentrations of HCHO gas may lead to pulmonary edema. It has been observed that HCHO gas present in workrooms at concentration ranges as low as 1 to 11 ppm can cause eye, nose, and throat irritation. HCHO is not only a potential carcinogenic chemical, but also it becomes a matter of concern due to sick house syndrome. HCHO concentration levels in domestic air in newly constructed houses vary from ambient level (1-25 ppbv) to as high as 4 ppm [1]. The regulated value in domestic air for HCHO in Japan is 100 μg m^{-3} (0.08 ppmv) [2]. HCHO is one of the products of incomplete combustion which is released to atmosphere: in metropolitan cities, formaldehyde is the predominant aldehyde emitted by automobiles especially when alcohol-based fuel was used [3] and also as a secondary product of photochemical reactions of volatile organic compound. Therefore, a rapid, simple and on-site method for its monitoring is urgently required.

A large number of methods for the determinations of HCHO in aqueous solutions have been reported so far. One of the flow-based methods is HPLC coupled with a derivatization reaction with 2,4-dinitrophenylhydrazine (DNPH) [4-6]. HPLC procedures, however, require long analysis times and are less sensitivity. Other methods, such as gas chromatography [7], potentiometry [8], biosensors [9], voltammetry [10], fluorometry [11-12] and spectrophotometry [13-17], have also been reported for the determination of HCHO. For spectrophotometry and fluorophotometry, a so-called Hantzsch reaction, which involves the cyclization of amine, aldehyde and β-diketone to form a dihydropyridine derivative, has often been used for spectrophotometric detection of HCHO in aqueous solutions. Nash [18] introduced a spectrophotometric method for HCHO determination, which was based on the Hantzsch reaction of HCHO with acetylacetone in the presence of ammonia. Compton and Purdy [19] proposed a reaction between HCHO and 4-amino-3-penten-2-one (Fluoral P), which can produce 3,5-diacetyl-2,6-dihydrolutidine. Fluoral P was subsequently used for the detection of formaldehyde [20-22].

A number of flow injection (FI) methods have been developed for the determination of HCHO in aqueous solutions. Gámiz-Gracia *et al.* [23] 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 5,5-dimethylcyclohexane-1,3-dione (dimedone) [24] and acridine yellow-bromate [25].

Basically, to determine HCHO gas samples have to be collected by bubbling air samples through an absorbing solution, followed by a chemical analysis. Several kinds of devices for HCHO collection have been developed including diffusive sampling device [26, 27] and gas diffusion scrubbers [28-29]. However, these instruments are large-scale, expensive and complicate, and furthermore the collection of gaseous analytes is not quantitative: the collection efficiency is usually less than 5-40%.

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In this work, a portable FI system, consisting of a pumping system, a sample injection valve, a reaction coil, a heating system and LED detector, was coupled with a simple batchwise sample collection method, and HCHO in air was determined. HCHO in air was easily collected in a small volume of an absorbing solution, which was analyzed by measuring the concentration of HCHO in the absorbing solution. The proposed method, utilizing acetylacetone reaction as a detection system, could be applied to the determination of trace amounts of HCHO in air.

2. Experimental

2.1. Apparatus

A schematic diagram of a portable type FIA system which was developed by Motomizu *et al.* [30-31], and now commercially available (F. I. A. Instrument, PFA-3000, Japan) is shown in Fig. 1. A double-plunger pump, P, was used for propelling a reagent (RS) and a carrier (CS) solution. A six-way valve, V, with a sample loop (200 μl) was used for introducing standard HCHO aqueous solutions, as well as sample solutions, into the carrier stream. PTFE tubing (0.5 mm i.d.) was used for flow lines, except for the back-pressure coil (0.25 mm i.d. tubing). The absorbance was measured using a LED detector, which consists of a diode, a flow cell, an interference filter (450 nm) and a light emitting diode (LED) as a light source. The light path of the flow cell was 10 mm and the volume 8 μl. The flow signals were recorded with a notebook computer system (FIA monitors; F. I. A. Instruments, Japan). All of the system components of the portable FIA, except for the recording apparatus, are packed in a small box (16 cm width x 16 cm height x 32 cm depth), and work with a 12 V battery. The proposed system is equipped with a controller for the adjustment of a flow rate, temperature of the reaction coil and a dynamic range of the detector. Therefore, the system can be used for on-site, real time measurement of HCHO by coupling with the batchwise on-site collection of HCHO in air.

A pH meter (Mettler Toledo, MP220, Switzerland) was used for adjusting pH of the reagent solution.

2.2. Reagents

All chemicals used in this work were of analytical reagent grade, and the water purified with a Milli Q Labo (Millipore, Japan) was used for the preparation of all solutions. The reagent solution, RS1, 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 adjusting pH. An acetylacetone stock solution was prepared by diluting 5.0 ml of acetylacetone (Wako Pure Chemicals, Osaka, assay min. 99.0%) with 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, Osaka) in the purified water and diluting it to 250 ml with the purified water.

A 1 M fluoral P stock solution was prepared by dissolving 1.0 g of fluoral P (Tokyo Kasei, Tokyo) in 10 ml of acetonitrile. A 0.4 M phosphate buffer solution (pH 6.0) was prepared by dissolving 42.6 g of dipotassium hydrogen orthophosphate and 20.5 g of potassium dihydrogen orthophosphate in about 900 ml of purified water, adjusting the pH to 6.0 with 0.1 M orthophosphoric acid and diluting to 1 l with purified water. The reagent solution, RS2, was prepared by diluting fluoral P stock solution with 0.4 M phosphate buffer solution (pH 6.0) to give a 0.1 M fluoral P solution.

A 0.10 M standard stock solution of HCHO was prepared by diluting 4.5 ml of 36.0-38.0% HCHO solution (Wako Pure Chemicals, Osaka) to 1000 ml with the purified water, followed by an accurate concentration determination using the iodometric method. The working standards were daily prepared by accurate dilution of the standard stock solution.

2.3. Procedures

2.3.1. Flow injection procedure

In Fig. 1, the each flow rate of double plunger pump, P, was set at 0.4 ml min^{-1}. The sample or standard solutions were injected into the carrier stream (purified water), then it was merged with the reagent stream, and flowed into a 5 m of 0.5 mm i.d. reaction coil which was heated at 70 °C in a heating compartment installed in the system. Absorbance changes of the reaction product were measured by visible absorption LOD detector (450 nm). The flow signals were recorded with a notebook-type computer and calculated the concentration of HCHO in air sample.

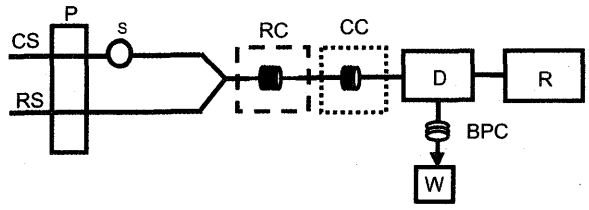

Fig. 1 Schematic portable flow injection system for formaldehyde determination. RS, reagent solution (0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0 or 0.1 M fluoral P solution in 0.4 M phosphate buffer at pH 6.0); CS, carrier solution (purified water); P, double-plunger pump (each flow rate: 0.4 ml min^{-1}); S, sample injection (300 μl); RC, reaction coil (0.5 mm i.d. x 500 cm); CC, cooling coil (0.5 mm i.d. x 50 cm); D, detector (LED as light source); R, recording system (PC); BPC, back-pressure coil (0.25 mm i.d. x 30 cm).

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

The concentrations of HCHO in the absorbing solutions were evaluated by the proposed FIA system (Fig. 1) with enough sensitivity and accuracy.

The batchwise collection of HCHO from air samples into the absorbing solution was investigated as follows. Accurate volumes of 50-ml plastic syringes as an air sampling vessel was measured by weighing the maximum volume of water filled in the syringes. The mean volumes (± standard deviation) of the syringes were found to be 71.92±0.43 ml (n=10), when the piston stopped at the end of the syringes. The results suggest that the volumes of the syringes are very reproducible and these syringes can be used as the air sampling vessel with enough accuracy. Three milliliters of the absorbing solution (the purified water) was transferred into the plastic syringes using a piston-type pipette (Eppendrof, 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 sampled into the vessels, and then the vessels were capped again. The sampling vessels were shaken

vigorously by hand for 4 min; then each absorbing solution was introduced into the FIA system using a six-way injection valve (300 μl) for HCHO measurement. The concentrations of HCHO in air samples can be calculated from the concentration of HCHO in the absorbing solution using the collection efficiency and the concentration factor of HCHO. In this experiment with the 50-ml syringe, the actual concentration factor was V_{air}/V_{abs} = 68.92/3.00 = 22.97, where V_{air} and V_{abs} represent the volume of the air sample (68.92 = 71.92-3.00 ml) and the absorbing solution (3.00 ml), respectively.

3. Results and discussion

3.1. Experimental variable for FIA system

The optimization experiments were performed by the FIA manifold in Fig. 1. The reaction between HCHO with acetylacetone or fluoral P requires relatively high temperature and long reaction time. The effect of the temperature on the signal intensities was examined by varying temperature from 25 to 70 °C using the heating system installed in the system (PFA-3000): the maximum available temperature of the system is 70 °C. In the procedure with acetylacetone as a reagent solution, the acetylacetone and ammonium acetate concentrations of the reagent solution were kept constant at 0.03 M and 1.5 M, respectively. The pH of the reagent solution was maintained at 6.0. The results (Fig. 2, a) show that the peak height increased sharply with an increase in temperature. When fluoral P was used as the reagent solution (Fig. 2, b), the same phenomenon was observed. Thus, a temperature of 70 °C was chosen for further studies.

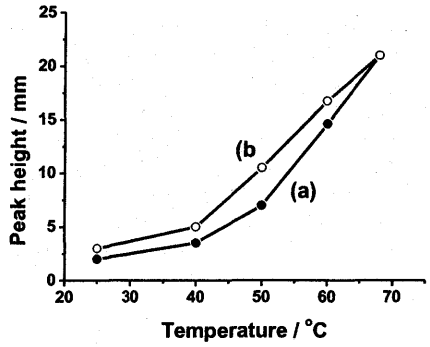

Fig. 2 Effect of reaction temperature on signal intensity. Sample, $1x10^{-5}$ M formaldehyde, sample volume, 300 μl; reagent, (a) 0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0 (b) 0.1 M fluoral P in 0.4 M phosphate buffer at pH 6.0.

The effect of reaction coil length was also examined in the range of 1 to 5 m using acetylacetone as a reagent solution. Figure 3 shows that the 5 m coil length gave the highest peak height; very similar results were obtained using the fluoral P reagent. Thus, 5-m coil length was used for further experiments.

The effect of flow rate in the range of 0.30-0.70 ml min^{-1} was investigated. The results obtained (Fig. 4) indicate that the peak intensity decreases with increasing flow rate because of insufficient reaction. As a compromise between sensitivity and analysis time, each flow rate of 0.4 ml min^{-1} was adopted for further studies.

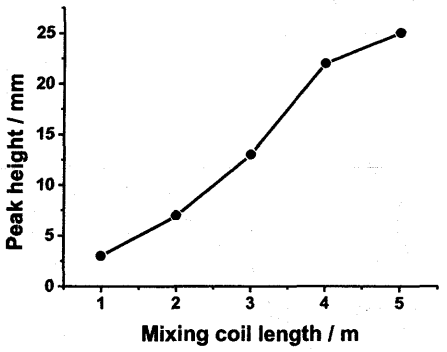

Fig. 3 Effect of mixing coil length on signal intensity. Sample, $1x10^{-5}$ M formaldehyde; sample volume, 200 μl; reagent solution, 0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0.

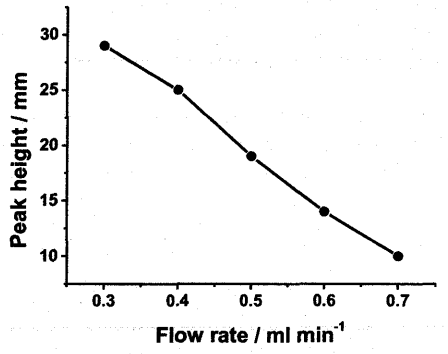

Fig. 4 Effect of flow rate of FI system on signal intensity. Sample, $1x10^{-5}$ M formaldehyde; sample volume, 200 μl; 0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0.

The sample injection volume was studied in the range of 100-500 μl under the optimum conditions. Figure 5 showed that the peak intensity increased with increasing of sample volume up to 200 μl, beyond which peak height remained constant. Thus, a sample volume of 200 μl was used for rapid measurement.

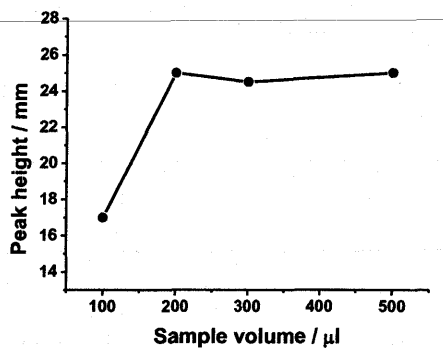

Fig. 5 Effect of sample injection volume of FI system on signal intensity. Sample, $1x10^{-5}$ M formaldehyde; 0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0.

The effect of pH on the reaction of formaldehyde with acetylacetone or fluoral P was examined: the results are shown in Fig. 6. The highest reaction efficiency was obtained at around pH = 6 both with acetylacetone and fluoral P.

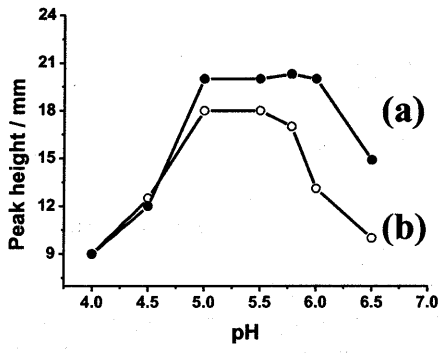

Fig. 6 Effect of pH on signal intensity. Sample, $1x10^{-5}$ M formaldehyde; sample volume, 200 µl; 0.1 M fluoral P in 0.4 M phosphate buffer, (a) acetylacetone in 1.5 M ammonium acetate (b) fluoral P in 0.4 M phosphate buffer.

The effect of the concentration of the reagent, acetylacetone and fluoral P, was examined. The results are shown in Fig. 7. The higher the concentration of the reagent, the higher the reaction efficiency becomes. As a compromise, 0.03 M of acetylacetone and 0.10 M of fluoral P were used.

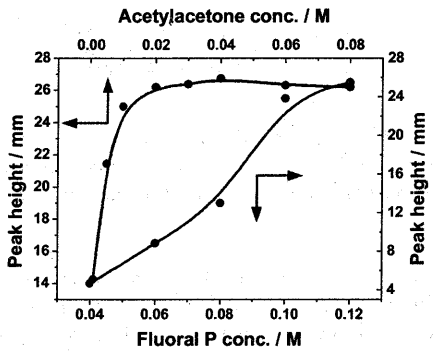

Fig. 7 Effect of acetylacetone in 1.5 M ammonium acetate and fluoral P concentration fluoral P in 0.4 M phosphate buffer on signal intensity. Sample, $1x10^{-5}$ M formaldehyde; sample volume, 200 µl.

3.2. Experimental variables for collection by batchwise method

The effect of shaking time on the absorption efficiency of HCHO from air sample into purified water was examined from 30 s to 7 min, using 3.00 ml of the purified water as an absorbing solution in a 50-ml plastic syringe (volume = 71.92±0.43 ml). The result obtained (Fig. 8) 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 as shaking time. In addition, the effect of standing time after sampling was tested: the results showed that the intensity remained constant even after standing it for more than 8 h. Therefore, the samples sampled on-site can be measured within 8 h.

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 with the same air sample. The results obtained indicate that in the first collection, the collection efficiency was more than 99%, while in the second and the third collection, the both efficiency were less than 0.5%. The signals obtained in the second and third procedures were very close to the background level. Such results suggest that HCHO in the 50-ml air sample could be quantitatively absorbed almost 100% in 3 ml of water in a single collection.

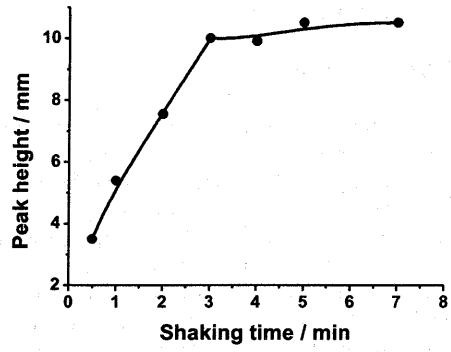

Fig. 8 Effect of shaking time on the collection of formaldehyde in the absorbing solution. Air sample, sampled at our laboratory on May 25, 2004; absorbing solution, milli Q water; 0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0.

3.3. Analytical characteristics

In this work, the standard aqueous solutions of HCHO were used for preparing the calibration graph at the concentration range of $1\text{-}20x10^{-6}$ M. The peak profile of HCHO is shown in Fig. 9. The equation of the calibration graph was expressed as A = 22.2C + 0.52, where A was peak height in mm and C was HCHO concentration in 10^{-6} M. The correlation coefficient was 0.9988 and the relative standard deviation (RSD) was 0.63% for $1x10^{-5}$ M HCHO (n = 12). The limit of detection (LOD) was $2.7x10^{-8}$ M in the absorbing solution (S/N = 3), which corresponds to 35 pptv of formaldehyde in air, and sample throughput of 60 injections h^{-1} was attained.

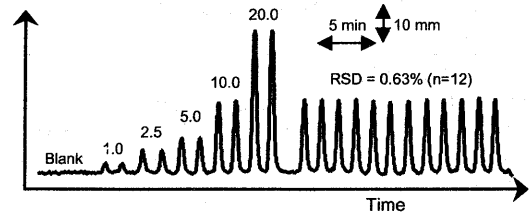

Fig. 9 Flow signals for formaldehyde determination in the range of $1\text{-}20x10^{-6}$ M. Reagent solution, 0.03 M acetylacetone in 1.5 M ammonium acetate at pH 6.0; sample volume, 200 µl; reaction temperature, 70 °C, reaction coil, 5 m x 0.5 mm i.d.; flow rate, 0.4 ml min^{-1}.

3.4. Application to real air samples

The proposed method was applied to the determination of HCHO in indoor and outdoor air. The results obtained by the proposed method are shown in Table 1. The proposed method was also applied for the

determination of HCHO in air as real-time monitoring. The outdoor air and indoor samples were collected into the sampling vessels (syringes), and were analyzed within 5 min. Figure 10 shows the results obtained. It was noted that low level of HCHO were observed under cloudy weather. The observed HCHO concentration fluctuations depended on the amount of mobile exhaust gas emitted. Further application of the proposed system to environmental analysis of ambient air will be performed under various climate and temperature conditions.

Table 1 Analytical results of formaldehyde in indoor and outdoor air

Sampling location	Date of sampling	HCHO[a] / ppbv
Laboratory	22 May 2004	7.58
Laboratory	25 May 2004	3.81
Living room A	26 May 2004	1.26
Living room B	26 May 2004	3.49
Living room C	26 May 2004	1.10
Living room D	26 May 2004	1.90
Outdoor air A	22 May 2004	3.70
Outdoor air B	25 May 2004	5.62

a Air sample volume, 68.9 ml; absorbing solution: 3 ml of purified water

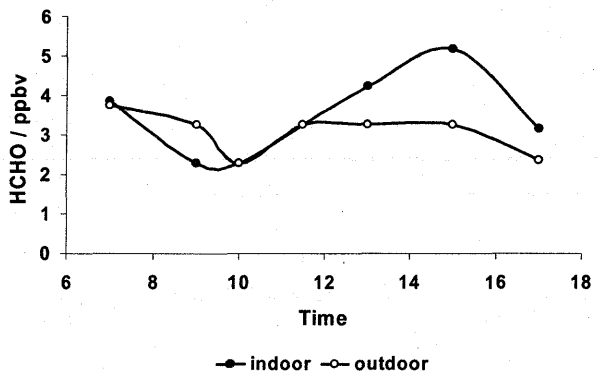

Fig. 10 Results obtained for HCHO monitoring. Air samples were collected at the cross road near the main gate of Okayama University and our laboratory on June 3, 2004. It was fine all day.

4. Conclusion

In the present work, a simple and rapid portable flow injection system for the determination of HCHO in the environmental air samples was developed. The HCHO 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. The LOD was 2.7×10^{-8} M (0.8 ppb). The proposed system provides the key advantages such as simpler and compact apparatus for HCHO analysis compared to other methods, low cost, and good portability for on-site/field measurements because the instrument is powered by a 12 V battery. The use of gas standard is also avoided. The proposed method can potentially be used for real-time monitoring of HCHO at low levels in air.

Acknowledgements

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