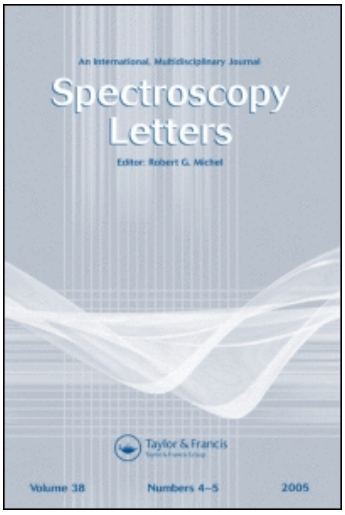


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectrophotometric Method with Silica-Gel Beads for Determination of Trace Formaldehyde in Air

Hong-yan Yuan[a]; Sheng-e Wang[a]; Dan Xiao[a]
[a] College of Chemical Engineering, Sichuan University, Chengdu, People's Republic of China

To cite this Article Yuan, Hong-yan , Wang, Sheng-e and Xiao, Dan(2005) 'Spectrophotometric Method with Silica-Gel Beads for Determination of Trace Formaldehyde in Air', Spectroscopy Letters, 38: 2, 121 — 130
To link to this Article: DOI: 10.1081/SL-200049571
URL: http://dx.doi.org/10.1081/SL-200049571

Spectroscopy Letters, 38: 121–130, 2005

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1081/SL-200049571

Spectrophotometric Method with Silica-Gel Beads for Determination of Trace Formaldehyde in Air

Hong-yan Yuan, Sheng-e Wang[†], and Dan Xiao
College of Chemical Engineering, Sichuan University, Chengdu, People's Republic of China

Abstract: A novel method is described for the determination of formaldehyde, with sensitivity enhancement based on the Hantzsch reaction, which involves the cyclization of ammonium, formaldehyde, and 2,4-pentanedione (PD) in Nash's reagent to form the yellow compound 3,5-diacetyl-1,4-dihydrolutidine (DDL) at pH 6. Silica-gel beads are added into solution, and the reaction completes within 55 min at room temperature without heating. The silica-gel beads not only catalyze the reaction process but also increase the sensitivity of the analysis. The proposed method is simple and convenient. The absorbance at 412 nm is proportional to the concentration of formaldehyde over the range of $0.1–2.0\,g \cdot mL^{-1}$. The detection limit is $0.1\,g \cdot mL^{-1}$. This method has been applied to the determination of formaldehyde in air with satisfactory results.

Keywords: Formaldehyde, 2,4-Pentanedione (PD), Silica-gel bead, Spectrophotometry

[†]On leave from Hunan University.

Received June 29, 2004, Accepted November 16, 2004

This paper was invited as a contribution to a special issue of the journal concerning Chemical Spectroscopy in China. It was presented at Sichuan University, Chengdu, China, October 17–24, 2003: the 6th International Symposium on Green Chemistry in China.

Address correspondence to Dan Xiao, College of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China. Fax: 86-28-85407859; E-mail: xiaodan99@sohu.com

INTRODUCTION

Formaldehyde is a colorless gas and is common in everyday life and industry. On one hand, it is used as a preservative in many foods to protect protein from deterioration. On the other hand, formaldehyde is now recognized as one of the most important and well characterized indoor air pollutants because of the extensive use of formaldehyde-containing construction and furnishing materials in modern structures and furniture. Owing to its toxicity and possible carcinogenic properties, formaldehyde is a concern of the occupational safety and health organization (OSHO) of many countries. Furthermore, formaldehyde is one of the widely used chemicals in the plastics industry, thus it is necessary to monitor its content in industrial applications. Therefore, a simple, highly sensitive, and extremely cost-effective analytical method for formaldehyde is desired and would be of tremendous benefit to many fields.

Indeed, a variety of methods have been developed for determination of formaldehyde. A wide range of chromatographic methods have been developed for the determination of formaldehyde after its transformation into stable derivatives.[1–6] In addition, formaldehyde in aqueous solutions can be determined by voltammetry.[7–9] These methods are sophisticated, and the sensitivities need to be improved. For example, the method of liquid chromatographic requires a fairly elaborate analytical procedure and a long measuring time per sample. The most widely used methods for the determination of formaldehyde are spectrophotometric methods.[10–12] Fluorimetry is particularly attractive for trace measurements because of its intrinsic sensitivity. Kiba et al.[13] immobilized the enzyme formaldehyde dehydrogenase (FDH) on poly (vinyl alcohol) beads, and such a bead-packed column was incorporated into a flow-injection system for the determination of low levels of formaldehyde in drinking water. Although the method is quite selective, the enzyme is expensive. Recently, Dasgupta et al.[14] developed a diffusion scrubber and light-emitting diode liquid-core waveguide–based fluorimetry for the measurement of atmospheric formaldehyde. The main problem of the method is interference from H_2O_2.

2,4-Pentanedione (PD) colorimetry has successfully been used for formaldehyde determination.[12] With pH 6 and ammonium, formaldehyde and 2,4-pentanedione are rapidly cyclized to form the yellow derivative 3,5-diacetyl-1,4-dihydrolutidine (DDL), which can easily be detected by spectrophotometry at 412 nm. As a comparison, PD colorimetric method is mentioned

Table 1. The experimental procedure

	1	2	3	4	5	6	7
PD solution (mL)	4.90	4.80	4.60	4.20	3.80	3.40	3.00
5.0 $\mu g \cdot mL^{-1}$ formaldehyde (mL)	0.10	0.20	0.40	0.80	1.20	1.60	2.00

as "standard method" in the experiment. In order to simplify further this method, a simpler spectrophotometric method, which applied silica-gel beads as a catalyst in the reaction at room temperature, was developed in this paper. This procedure is much simpler and more convenient, and the sensitivity is much improved. The method has been applied to the determination of formaldehyde in air with satisfactory results.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were carried out with a TU-1901 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China), and the absorption spectra were recorded with a personal computer. A mass spectrometer (LCQ^{TM} DECA Finnigan, California, USA) was used for characterizing the products.

Reagents

Stock solution of formaldehyde was prepared from purchased aqueous formaldehyde solution (37.0–40.0%) and standardized by the iodometric method. 2,4-Pentanedione was further purified by distillation before use and kept in the dark. PD solution was prepared by dissolving 25 g of ammonium acetate, 3.0 mL of 70% acetic acid solution, and 0.2 mL of freshly distilled PD in water in a 100-mL volumetric flask. Diluted solutions of formaldehyde and PD were freshly prepared prior to use as described in Table 1. All reagents were of analytical reagent grade. Deionized distilled water was used throughout the experiment.

Procedure

An appropriate amount of the PD, silica-gel beads, and 5.0 $\mu g \cdot mL^{-1}$ formaldehyde solution was transferred into a 5-mL colorimetric tube, mixed, and the stood at room temperature for 55 min to form the derivative. Yellow reaction solution (pH = 6.2) was obtained, and absorbance was measured at the wavelength of 412 nm.

RESULTS AND DISCUSSION

Absorption Spectrum

The absorption spectra of the reaction solutions presented a maximum at 412 nm (Fig. 1), which conformed to the standard method.[12] As the

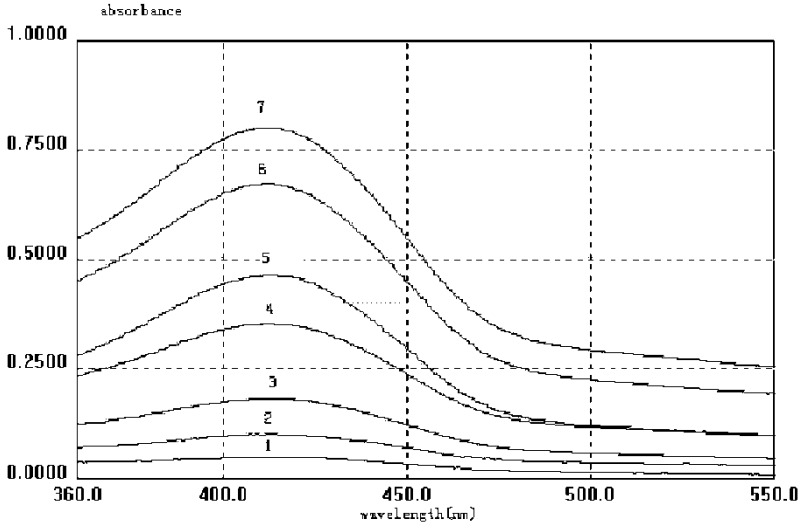


Figure 1. Ultraviolet-visible spectra of the reaction solutions at different formaldehyde concentrations. (1) $0.1\,\mu g \cdot mL^{-1}$; (2) $0.2\,\mu g \cdot mL^{-1}$; (3) $0.4\,\mu g \cdot mL^{-1}$; (4) $0.8\,\mu g \cdot mL^{-1}$; (5) $1.2\,\mu g \cdot mL^{-1}$; (6) $1.6\,\mu g \cdot mL^{-1}$; and (7) $2.0\,\mu g \cdot mL^{-1}$.

concentration of formaldehyde increased, the corresponding peak absorbance increased proportionally, as shown in Fig. 1.

Working Curve and Sensitivity

Standard solutions of formaldehyde (0.1, 0.2, 0.4, 0.8, 1.2, 1.6, and $2.0\,\mu g \cdot mL^{-1}$) were measured, and a calibration curve is shown in Fig. 2.

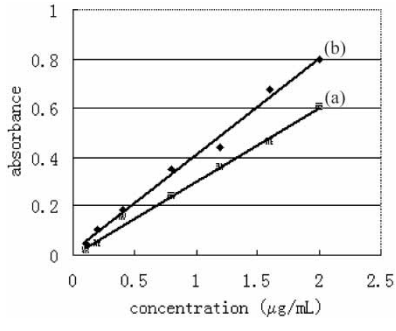


Figure 2. Calibration curves of the two methods. (a) The standard method; (b) the proposed method.

The calibration curve is based on the average of three determinations of each standard solution obtained in a measuring cycle every 10 min. In the standard procedure, the amount of HCHO in the range 0.1–2.0 $\mu g \cdot mL^{-1}$ obeys Beer's law. The fitted equation is

$$A = 0.019 + 0.393C_{HCHO} \quad (1)$$

where A is absorbance, C_{HCHO} denotes the concentration of HCHO $\mu g \cdot mL^{-1}$, and the correlation coefficient is 0.9964 ($n = 7$). In the case of the standard method,[12] the linear regression equation for the 0.1–2.0 $\mu g \cdot mL^{-1}$ range is

$$A = -0.0003 + 0.300C_{HCHO} \quad (2)$$

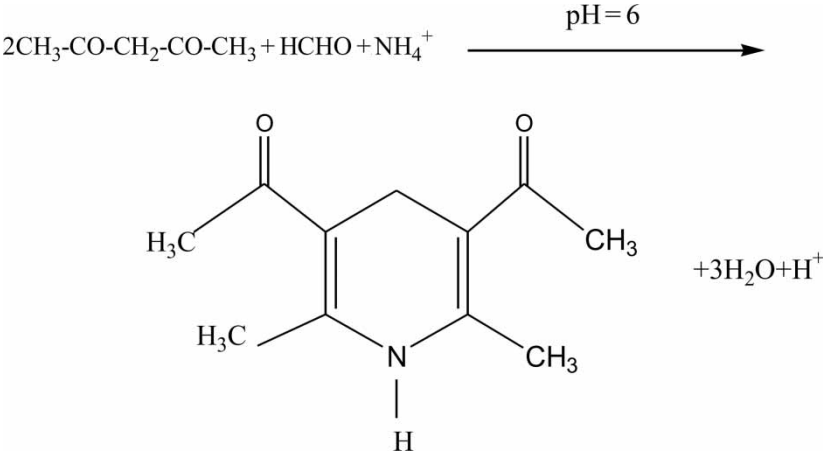
The correlation coefficient is 0.9972 ($n = 7$). Because the slope of Eq. (1) is larger than that of Eq. (2), it can be concluded that the sensitivity of the proposed method is much improved. It was estimated that the detection limit of the proposed method for HCHO was 0.1 $\mu g \cdot mL^{-1}$.

Stability

The reaction time dramatically affects the observed analytical signal. Figure 3 shows the dependence of absorbance on the reaction time upon addition of 0.4 $\mu g \cdot mL^{-1}$ HCHO under otherwise identical conditions. Absorbance increases with elongated reaction time. But when the reaction time is more than 55 min, the absorbance displays a plateau. Based on these results, the reaction time of 55 min was chosen.

Mechanism of Reaction Process

It was reported that the reaction could be described as follows:[15]



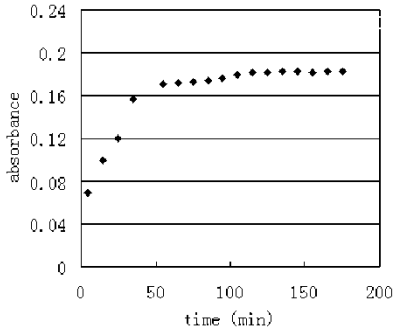


Figure 3. Dependence of the analytical signal upon reaction time.

The Hantzsch cyclization requires the elimination of three water molecules, and the reaction temperature and time has a pronounced effect on the reaction rate. It was reported that aldehydes reacted completely in 1 hr at 60°C,[16] 3 min at 100°C,[17] and 12 min at 51°C[15] with water bath. However, the results obtained with the proposed method showed that formaldehyde reacted completely in 55 min at room temperature in the presence of silica-gel beads, indicating that the reaction rate is greatly improved by silica-gel beads. In order to achieve stable color of the reaction solution in the same conditions, a larger amount of silica-gel beads are needed for higher concentration of formaldehyde. It shows that the surface area of the silica-gel beads affects the reaction rate significantly, which appears to be associated with the catalysis effect on the reaction rate. In addition, the peak absorbance of the proposed method is also stronger than that of

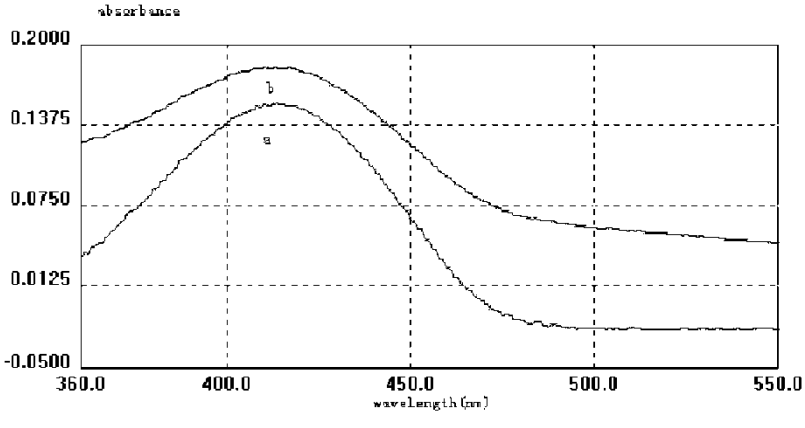


Figure 4. Ultraviolet-visible spectra of the reaction solution with the two methods. (a) The standard method; (b) the proposed method.

the standard method,[12] as shown in Fig. 4, and this can be attributed to the producing of new component. The products that are synthesized with the standard method and the proposed method were identified by Mass Spectrometry (MS), and the MS spectra of the derivatives of formaldehyde are shown in Fig. 5. The $[M+H]^+$ ion with m/z 192 is base peak, and the $[M+H]^+$ ion is the dominant peak in any of the individual mass spectra. The peaks near m/z 206 are detected only with the products of the proposed

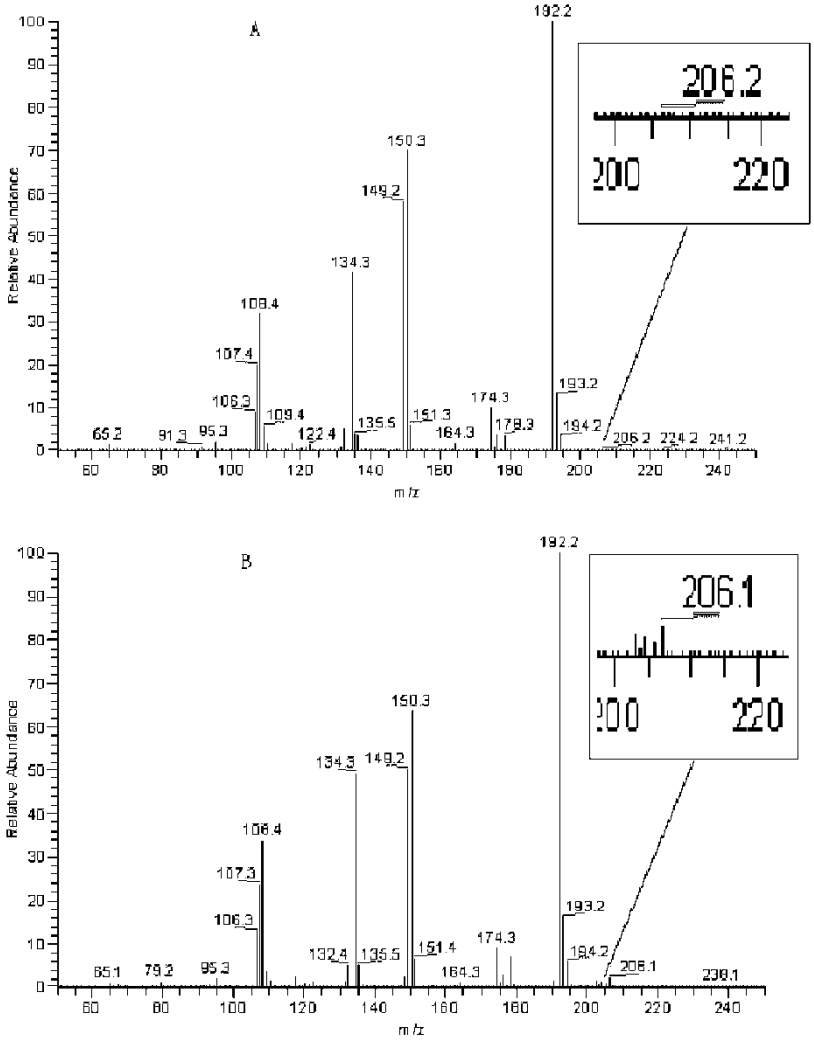


Figure 5. MS spectra of the formaldehyde derivatives obtained with the standard method (A) and the proposed method (B).

method as shown in Fig. 5B and not of the standard method as shown in Fig. 5A. The peaks may be interpreted as the other species, which may contribute to the absorption of the region 480–550 nm, produced in the reaction process with the proposed method. A possible explanation for the results is that silica-gel beads accelerated the reaction process as a catalyst, and that silica-gel beads reacted with one of the reaction reagents to form a new component, which reacted easily with the other reaction reagents to form the derivative (DDL) by cyclization at room temperature. However, further research is needed to understand fully the new constitution.

Specificity of the Derivatization Reaction and Interferences

According to the report,[15] 2,4-pentanedione does not react with ketones, and the only aldehydes it reacts with are formaldehyde and acetaldehyde. Therefore, the current method is a fairly selective method, and the effect of acetaldehyde on the method ought to be explored. An interference study was carried out by quantifying the effect of acetaldehyde on detection of formaldehyde. Five milliliters of the standard solution containing $0.4\,\mu g \cdot mL^{-1}$ formaldehyde was analyzed. The result was compared with that of containing $0.4\,\mu g \cdot mL^{-1}$ formaldehyde and $6\,mg \cdot mL^{-1}$ acetaldehyde in 5 mL, and the relative error was 4.4%. This low relative error revealed that $6\,mg \cdot mL^{-1}$ acetaldehyde did not present strong impact on the determination of formaldehyde. A similar study was carried out for the standard method,[12] however, the relative error was 41%, which is much greater than that of the proposed method. Although the sensitivity was enhanced, the increased blank was significant.

Sample Analysis

The proposed method was applied to the determination of trace amount of formaldehyde in air. Formaldehyde was collected in newly decorated rooms by an active sampler using a pump and bubbler and then analyzed by the procedure already described under "Experimental". The results from the proposed method agreed well with those obtained by the standard method[12] (Table 2). The relative errors for samples detection were better than 5%.

Table 2. Determination of formaldehyde in air samples

Sample	Proposed method (n = 6) ($mg \cdot m^{-3}$)	Reference method ($mg \cdot m^{-3}$)
A (A newly decorated room)	0.515 ± 0.0029	0.496 ± 0.0048
B (Another newly decorated room)	0.456 ± 0.0024	0.436 ± 0.0047

CONCLUSIONS

Trace formaldehyde can be determined by the proposed spectrophotometric method. The sensitivity is enhanced, and the method can be operated simply and easily without heating. Furthermore, without heating and cooling to room temperature, the reaction and measurement can be carried out at the same time, thus the proposed method may potentially be used to make a monitoring sensor for formaldehyde. Research work on the sensor is in progress in this research laboratory.

REFERENCES

1. Muntuta-Kinyanta, C.; Hardy, J. K. Permeation-solid adsorbent sampling and GC analysis of formaldehyde. *Talanta* **1991**, *38* (2), 1381–1386.
2. Dalene, M.; Persson, P.; Skarping, G. Determination of formaldehyde in air by chemisorption on glass filters impregnated with 2,4-dinitrophenylhydrazine using gas chromatography with thermionic specific detection. *J. Chromatogr.* **1992**, *626* (2), 284–288.
3. Levin, J.-O.; Andersson, K.; Lindahl, R.; Nilsson, C.-A. Determination of sub-part-per-million levels of formaldehyde in air using active or passive sampling on 2,4-dinitrophenylhydrazine-coated glass fiber filters and high-performance liquid chromatography. *Anal. Chem.* **1985**, *57* (6), 1032–1035.
4. Medvedovici, A.; David, V.; David, F.; Sandra, P. Optimization in the formaldehyde determination at sub-ppm level from acetals by HPLC-Dad. *Anal. Lett.* **1999**, *32* (3), 581–592.
5. Kaminski, J.; Atwal, A. S.; Mahadevan, S. High performance liquid chromatographic determination of formaldehyde in milk. *J. Liq. Chromatogr.* **1993**, *16* (2), 521–526.
6. Bechmann, I. E. Determination of formaldehyde in frozen fish with formaldehyde dehydrogenase using a flow injection system with an incorporated gel-filtration chromatography column. *Anal. Chim. Acta* **1996**, *320* (2–3), 155–164.
7. Chan, W. H.; Chung, W. C.; Cai, P. X. Differential-pulse polarographic microdetermination of formaldehyde via in situ derivatization with Girard's reagent T. *Analyst* **1995**, *120* (8), 2233–2236.
8. Chan, W. H.; Xie, T. Y. Adsorption voltammetric determination of $\mu g \cdot l^{-1}$ levels formaldehyde via in situ derivatization with Girard's reagent T. *Anal. Chim. Acta* **1997**, *39* (1–2), 173–179.
9. Wang, L.-H.; Chen, Z.-S. Determination of free formaldehyde in nail preparations by differential pulse voltammetry. *Electroanalysis* **1996**, *8* (8), 842–846.
10. Altshuller, A. P.; Miller, D. L.; Slega, S. F. Determination of formaldehyde in gas mixtures by the chromotropic acid method. *Anal. Chem.* **1961**, *33* (4), 621–625.
11. Sawicki, E.; Hauser, T. R.; Stanley, T. W.; Elbert, W. New methods for the detection, rapid estimation, and determination of aliphatic aldehydes. *Anal. Chem.* **1961**, *33* (1), 93–96.
12. Chui, J. S.; Wang, Q. Y.; Wang, H. P. *The Methods for Testing Atmospheric Pollution*, 2nd ed.; Chemical Industry Press: Beijing, 1997; p. 545 (in Chinese).

13. Kiba, N.; Sum, L.; Yokose, S.; Kazue, M. T.; Suzuki, T. T. Determination of nanomolar levels of formaldehyde in drinking water using flow-injection system with immobilized formaldehyde dehydrogenase after off-line solid-phase extraction. *Anal. Chim. Acta* **1999**, *378* (1–3), 169–175.
14. Li, J.; Dasgupta, P. K.; Genfa, Z.; Hutterli, M. A. Measurement of atmospheric formaldehyde with a diffusion scrubber and light-emitting diode-liquid-core waveguide based fluorometry. *Field Analytical Chemistry and Technology* **2001**, *5* (1–2), 2–12.
15. Jones, S. B.; Christopher, M. T.; Tedd, E. L.; David, C. J. Determination of submicromolar concentrations of formaldehyde by liquid chromatography. *Anal. Chem.* **1999**, *71* (18), 4030–4033.
16. Mopper, K.; Stahovec, W. L. Trace analysis of aldehydes by pre-column fluorigenic labeling with 1,3-cyclohexanedione and reversed-phase high-performance liquid chromatography. *J. Chromatogr.* **1983**, *256* (2), 243–252.
17. Fan, Q. J.; Dasgupta, P. K. Continuous automated determination of atmospheric formaldehyde at the parts per trillion level. *Anal. Chem.* **1994**, *66* (4), 551–556.