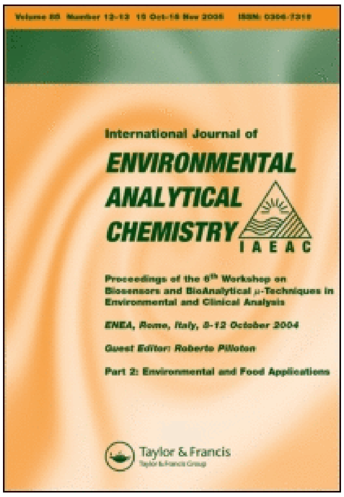

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Continuous Monitoring of Gaseous Formaldehyde Using an Improved Fluorescence Approach

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**To cite this Article** Kelly, T. J. and Fortune, C. R.(1994) 'Continuous Monitoring of Gaseous Formaldehyde Using an Improved Fluorescence Approach', International Journal of Environmental Analytical Chemistry, 54: 4, 249 — 263
**To link to this Article: DOI:** 10.1080/03067319408034093
**URL:** http://dx.doi.org/10.1080/03067319408034093

*Intern. J. Environ. Anal. Chem.*, Vol. 54, pp. 249-263
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# CONTINUOUS MONITORING OF GASEOUS FORMALDEHYDE USING AN IMPROVED FLUORESCENCE APPROACH

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*(Received, 24 March 1993; in final form, 14 May 1993)*

A continuous monitor for gaseous formaldehyde (HCHO) has been developed which avoids key limitations of previous monitors. The Hantzsch reaction, the cyclization of a β-diketone, an amine, and formaldehyde, is used to produce a fluorescent derivative from HCHO. Use of 254 nm light for excitation provides fluorescence sensitivity nearly four times that obtained previously with 406 nm excitation. This improvement in fluorescence sensitivity leads to a gaseous detection limit of 0.2 ppbv with a glass coil scrubber as the collection device for gaseous HCHO. The Hantzsch reaction provides high selectivity, high reagent stability, and low reagent cost, while the glass coil provides high efficiency, stability of behavior, and simplicity of design. The monitor consequently provides sensitive and specific measurement of gaseous HCHO in a reliable and simple device. The rise and fall times of the instrument response are both 80 seconds, with a lag time of 120 seconds. Repetitive calibrations during extended field operations indicate a reproducibility of about ± 7 percent (relative standard deviation). Ambient HCHO data from surface sites show strong diurnal variations, and measurements aboard an aircraft show a sharp vertical gradient in HCHO.

**KEY WORDS:** Formaldehyde, ambient air, indoor air, continuous monitoring, fluorescence.

## INTRODUCTION

Formaldehyde (HCHO) is the most abundant gaseous carbonyl compound in the ambient atmosphere, originating from primary emissions in combustion sources and from atmospheric oxidation of hydrocarbons. Formaldehyde produces free radicals upon photolysis by sunlight, contributing to the photochemical formation of ozone and other oxidants.[1] Formaldehyde is also found in indoor air, at levels typically several times higher than in outdoor air,[2] as a result of emissions from a variety of materials and products.[3] As a suspected human carcinogen, formaldehyde is an important toxic compound in both outdoor and indoor air. For these reasons, several methods have been devised for measurement of HCHO at the levels (ppm = $1 \times 10^{-6}$, to sub-ppb = $1 \times 10^{-9}$, by volume) typically present in air.[4]

The most commonly used method for gaseous HCHO is reaction with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone derivative, which is then separated by high pressure liquid chromatography and determined by UV absorption.[e.g., 5–8] This method can be deployed using DNPH in solution in impingers[6] or coated onto solid supports in sampling cartridges,[7,8] and provides measurements of other carbonyl compounds, as well as HCHO. However, it generally requires sampling intervals of a few hours to detect HCHO at levels down to 1 ppbv, such as are characteristic of ambient air. Direct spectroscopic methods for HCHO using FTIR,[9] tunable diode laser absorption spectroscopy,[10] and differential optical absorption spectroscopy[11] have also been developed. Spectroscopic methods have been used as reference standards in intercomparisons of HCHO measurements,[12,13] but all the spectroscopic methods use relatively large, complex, and costly instrumentation, which is not suitable for monitoring of HCHO in many environments of interest.

In order to achieve simple, sensitive, and rapid measurements of HCHO, small, portable, continuous wet-chemical monitors have been developed. The automated pararosaniline colorimetric method, long used for workplace monitoring of formaldehyde, has been modified to achieve a detection limit of 10 ppbv,[14,15] sufficient for indoor, but not outdoor, HCHO monitoring. More sensitive continuous HCHO monitors have been developed, based on fluorescence detection of derivatives produced by collection of gaseous HCHO and reaction with nicotinamide adenine dinucleotide in the presence of formaldehyde dehydrogenase enzyme,[16] or with a β-diketone via the Hantzsch reaction.[17,18] Both of these approaches can provide detection limits below 1 ppbv, and have been employed in ambient atmospheric monitoring of formaldehyde, but with certain limitations. The enzyme approach, though highly sensitive, suffers from reagent instability, relatively high reagent cost, and excessively long (i.e., several minutes) response time. The Hantzsch reaction approach has used membrane-based diffusion scrubbers as collectors of gaseous formaldehyde. These devices are relatively inefficient, and have been prone to unstable performance, apparently caused by accumulation of atmospheric particles on the scrubber surface, though designs which minimize the latter problem are being developed.[19]

The goal of the present work was to develop an improved continuous monitor for gaseous HCHO, capable of sub-ppbv detection limits, but free of the primary limitations of previous monitors. Development of the monitor included use in several field studies[20–23] including continuous airborne HCHO measurements over the eastern U.S. Examples from those measurements are presented to illustrate the utility of the device.

## EXPERIMENTAL

### *Selection of approach*

A literature review was conducted to evaluate four existing detection schemes for aqueous formaldehyde, and 11 collection devices suitable for continuously scrubbing formaldehyde from air.[20] The former review indicated that the Hantzsch reaction[17] provides the best combination of sensitivity, specificity, speed of response, simplicity and stability of reagents, and potential for improvement. The latter review indicated that a glass coil scrubber[16] provides the best combination of high efficiency, stability, simplicity, and ruggedness, but its relatively low air/water contact ratio requires a highly sensitive detection method for aqueous formaldehyde in order to achieve sub-ppbv gaseous detection limits. In the present study, a means of increasing the sensitivity of fluorescence detection of the product of the Hantzsch reaction was exploited, allowing such detection limits to be achieved with the glass coil scrubber.

The Hantzsch reaction is the multi-step cyclization of a β-diketone, an amine, and formaldehyde to produce a dihydropyridine derivative. This approach has been used for both colorimetric[24] and fluorescence[25] detection of HCHO, and the latter method is the basis for the continuous HCHO monitor developed by Dasgupta *et al.*[17,18] In common practice the fluorescence approach uses 2,4-pentanedione (i.e., acetylacetone) in ammonium acetate buffer, and the fluorescent product formed is 3,5-diacetyl 1,4-dihydrolutidine (DDL). In previous use of the Hantzsch reaction for fluorescence detection of HCHO, the excitation maximum at 410 nm was used, as suggested by the spectroscopic data for DDL shown by Belman.[25] Excitation at 410 nm has been obtained by use of phosphor-coated lamps, producing maximum light output at 406 nm.[17] However, a more powerful light source has been suggested as one way to increase detection sensitivity,[17] since the fluorescence efficiency of DDL is relatively low. This fact is the basis for the improvement of the Hantzsch approach in the present work. Specifically, review of the data of Belman[25] disclosed an absorption maximum for DDL near 254 nm, which was stronger than the 410 nm absorption, but which was not identified as an excitation maximum. Since the various spectra given by Belman were obtained on different instruments, it was not clear whether excitation at 254 nm had been adequately evaluated. Furthermore, it seemed possible that the high light intensity achievable at 254 nm from a mercury lamp might provide higher sensitivity than excitation at 410 nm, even if the excitation efficiency at 254 nm were relatively lower.

### *Wavelength comparison*

Comparison of 410 nm and 254 nm excitation with the Hantzsch reaction was done using a flow injection apparatus and reagent concentrations similar to those of Dong and Dasgupta.[17] A Sequoia-Turner Model 112 fluorometer with a quartz microvolume flow cell was used. Excitation at 254 nm was achieved with a low pressure mercury lamp (G4T4/1; BHK, Inc.), a 254 nm interference filter (20 percent peak, 10 nm FWHM) in the excitation path, and the combination of a GG-10 Schott glass filter (Corion, Inc.) and a 500 nm long-pass filter (Sequoia-Turner) in the emission path. The latter combination was found to be the optimum, of over 30 filters and filter combinations tested, in reducing fluorescence background caused by stray 254 nm light. Excitation at 410 nm employed a G4T4/1 lamp coated with a phosphor to emit at 406 nm (BHK, Inc.), a 410 nm interference filter (45 percent peak, 10 nm FWHM; Corion, Inc.), and a 470 nm long-pass filter (Sequoia-Turner). The analysis of $1 \times 10^{-6}$ and $1 \times 10^{-5}$ M HCHO solutions using both approaches disclosed that fluorescence response is nearly a factor of 4 greater with 254 nm excitation than with 410 nm excitation. Use of UV excitation was adopted for all subsequent work (U.S. Patent 5,132,227), and it was concluded that the increased sensitivity afforded by 254 nm excitation was sufficient to allow use of the glass coil as the collection device for gaseous HCHO.

### *HCHO monitor.*

Figure 1 is a schematic of the continuous HCHO monitor. The Turner fluorometer is used as described above, with a peristaltic pump (Gilson Minipuls 2) for circulation of reagent flows. The glass sampling coil is a 28-turn Technicon Auto Analyzer mixing coil of 3 mm I.D. (Alpkem Corp.), and is mounted with the coil axis oriented vertically. A scrubbing solution of 0.1 N $H_2SO_4$ is supplied to the entrance of the coil at a flow rate of approximately 0.7 mL/min, and flows down the coil concurrently with the sample air flow of 1–2 L/min. The acidity of the scrubbing solution serves both to promote rapid dissolution of gaseous HCHO, and to minimize the dissolution of gaseous $SO_2$, which otherwise could interfere by formation of a S(IV)-HCHO adduct in the aqueous phase. The concurrent air and scrubber solution flows are separated by gravity at the bottom of the glass coil, and the air flow is drawn off by a pump through a mass flow controller (Tylan Corp.). The scrubbing solution containing collected formaldehyde is mixed with a flow of 0.2 mL/min of a reagent consisting of 6 M ammonium acetate (anhydrous ACS reagent; Aldrich), 0.16 M acetic acid, and $1 \times 10^{-2}$ M 2,4-pentanedione (acetylacetone) (99 + %, Aldrich Gold Label). The

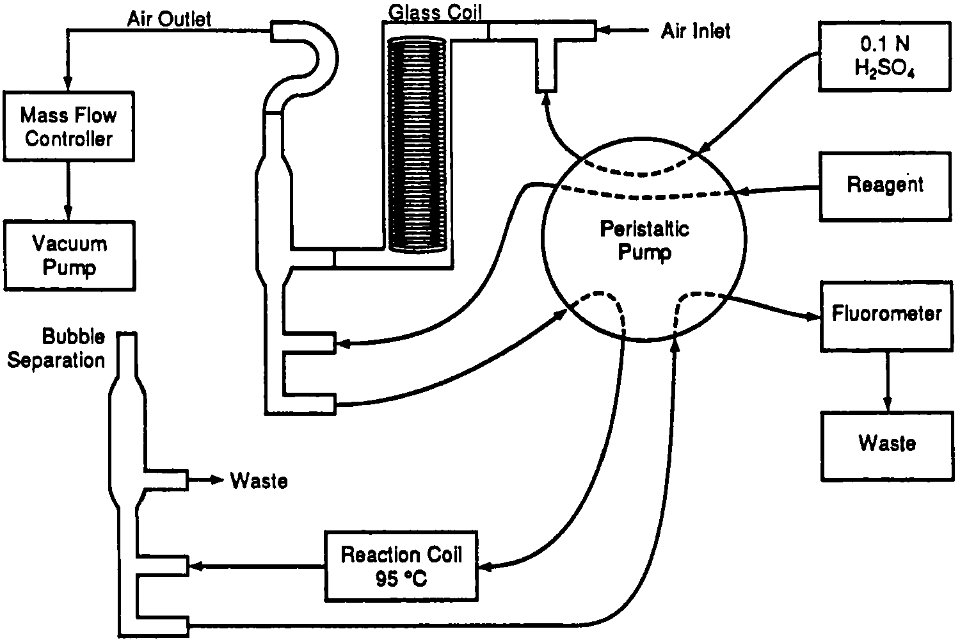

**Figure 1** Schematic of the continuous HCHO monitor.

combined aqueous flow is then pumped through a coil of 1/16-in. O.D. stainless steel tubing, maintained at 95 °C (± 1 °C). The 30-second residence time in this coil is sufficient to quantitatively convert the collected HCHO to the DDL derivative. The aqueous flow from the scrubber coil through the heated reaction coil is segmented with air bubbles to help retain concentration gradients and to scavenge bubbles produced by degassing in the heated zone. The solution leaving the heated reaction coil enters a debubbler and a final flow of bubble-free solution is pumped to the fluorometer for detection of the DDL product.

The reagent concentrations noted above were found to provide complete formation of the DDL product within the 30-sec passage through the heated coil, and provide reagent concentrations after mixing with the scrubber solution that are comparable to those in a previous monitor based on the Hantzsch reaction.[18] However, use of 254 nm excitation results in greater reagent background fluorescence than does 410 nm excitation. This background is greatly reduced by purifying the commercial 2,4-pentanedione by fractional distillation before use. Tests with a direct gas-phase HCHO source have shown the glass coil scrubber and 0.1 N $H_2SO_4$ scrubbing solution to be essentially 100 percent efficient for collection of gaseous HCHO at air flow rates up to 2.0 L/min.[20] As a result, aqueous calibration standards can be used in place of gaseous standards, provided the monitor is operated within that air flow range. Correct conversion of aqueous standards to gaseous equivalent concentrations requires accurate measurement of the scrubber solution flow rate entering the collection coil. HCHO standards in the $10^{-7}$ to $10^{-6}$ M range (equivalent to about 1–10 ppbv HCHO) are made up by serial dilution of 37 percent Formalin solution (Baker Analyzed) in the 0.1 N $H_2SO_4$ scrubber solution. Such standards have been found to be stable for at least 3 days. In extended operation they are typically made up from dilute stock solutions of $10^{-3}$ M HCHO. The monitor is zeroed by supplying high-purity air to the inlet, or by inserting an impinger containing the 0.1 N $H_2SO_4$ scrubbing solution into the sample air flow to remove HCHO upstream of the scrubber coil. Calibration solutions are ordinarily provided to the monitor by means of manual miniature valves in the flow streams. In a modification for field use, span and zero samples are provided to the monitor at regular intervals using automated valving.

## RESULTS AND DISCUSSION

Laboratory and field testing of the HCHO monitor have been conducted both in the development and subsequent use of the device by Battelle,[20,21,23] and in an independent evaluation by ManTech.[22] The field studies from which data are drawn for this paper are: (1) Short-Term Variations of Concentrations of Hazardous Air Pollutants in Urban Air (HAPS), conducted in Columbus, Ohio, in the summer of 1989; (2) the second Acid Model Operational Diagnostic Evaluation Study (Acid-MODES), a multi-aircraft study conducted in the eastern U.S. in the spring of 1990 for evaluation of regional acid deposition models; and (3) the Atlanta Ozone Precursor Study (OPS), conducted in the Atlanta metropolitan area in the summer of 1990. In the subsequent discussion these studies will be denoted by the abbreviations given here.

## *Analytical characteristics*

Figure 2 is a chart trace of the monitor's response to HCHO at ppbv levels in indoor air in our laboratories, illustrating both the sensitivity and time response of the monitor. A period of monitoring of room air containing approximately 5 ppbv formaldehyde is bracketed by two periods of zeroing the monitor with UHP air. The data shown were sampled from the continuous monitor by a laboratory data acquisition system at 15-second intervals. No averaging of the data was performed, except for a 10-second time constant imposed on the fluorometer output. A limit of detection of 0.2 ppbv is indicated by these data, based on three times the standard deviation of the blank signal, as was also found during extended field measurements.[20,22] This LOD is slightly higher than those achievable with previous continuous monitors,[16,18] but still more than sufficient for ambient atmospheric measurements, and is achieved with simple, stable reagents and an efficient, reliable scrubber design. The time response of the monitor consists of a lag time due to the flow system, and rise/fall times of a concentration front through the fluorometer. The lag time of the monitor is approximately 120 seconds, with rise and fall times (10% – 90% and 90% – 10%, respectively) of 80 seconds. The lag time of the present monitor is much shorter than that of previous monitors; [16,18] the rise/fall time is equivalent to that of the enzyme-based monitor,[16] and somewhat faster than that of the Hantzsch/diffusion scrubber approach.[18]

Day-to-day precision of the monitor is within 5 percent in laboratory operation, and similar behavior has been found in field studies. In the HAPS measurements, a total of 49 single-point calibrations were done using solutions equivalent to 2.6 to 13 ppbv, during a

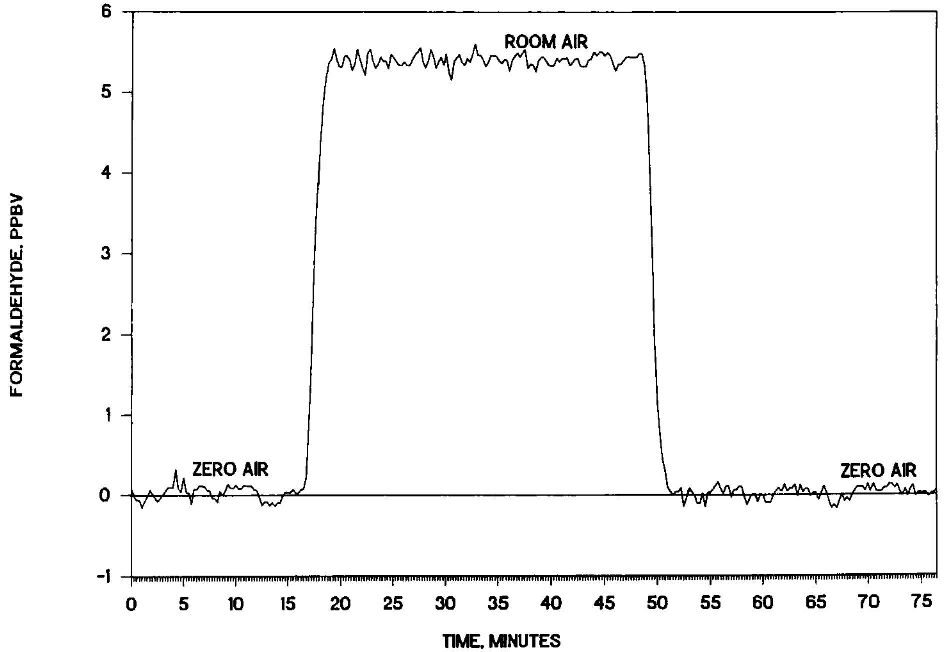

**Figure 2** Example of real-time monitor response to HCHO in room air.

15-day period of continuous operation. Reagent solutions and standards were prepared every second day. The relative standard deviation of response observed was 9.7 percent at 2.6 ppbv (N = 12), 7.6 percent at 5.3 ppbv (N = 13), and 7.0 percent at 13 ppbv (N = 22). In the OPS study, reagents and standards were prepared fresh every third day. In that study, four multi-point calibrations conducted during the 2-week field study, using solutions equivalent to 4.6 to 18.5 ppbv, provided linear slopes which averaged 62 (± 4.8) mV/ppbv, for a relative standard deviation of 7.7 percent. Automated span samples run in the OPS measurements produced a similar result: 62 runs of a nominal 11.1 ppbv equivalent standard produced a relative standard deviation of 6.1 percent, with an average bias of 0.4 ppbv (3.6 percent) from the nominal span value. Consideration of these field results with additional sources of uncertainty, such as gas and scrubber solution flow measurements, suggests that the absolute accuracy of the method is within about 15 percent.

The HCHO monitor has provided linear response in calibrations up to at least 1 ppmv with the stated reagent concentrations, though no effort has been made to define the upper limit of linear response with the present reagents. However, the monitor has also been used for monitoring of HCHO at higher ppmv levels,[21] by reducing sample flow and fluorometer settings from their optimum values. Linear response at those levels requires increasing the concentration of 2,4-pentanedione in the reagent solution.

### *Interferences*

Tests established that the specificity for HCHO found with the Hantzsch reaction using excitation at 410 nm is retained when using excitation at 254 nm. The selectivity of the monitor for formaldehyde was found in initial work[20] to be > 10,000 : 1 relative to acetaldehyde and > 2,000 : 1 relative to benzaldehyde. Subsequent tests showed no response to aqueous solutions containing the equivalent of 100 ppbv of acetaldehyde, acrolein, propionaldehyde, butyraldehyde, benzaldehyde, acetone, methyl ethyl ketone, methyl isobutyl ketone, formic acid, and methanol.[22] These tests confirm that the Hantzsch reaction is essentially specific for formaldehyde. Note that in atmospheric sampling, the collection of most potential interferents into the aqueous phase is likely to be less efficient than for HCHO, in part because of their lower gaseous diffusion coefficients. This factor further assures the selectivity of the method for HCHO.

### *Comparisons to other methods*

Measurements made with the HCHO monitor have been compared on several occasions with results from other methods. Table 1 shows a comparison of results from the present monitor with those from the improved pararosaniline monitor,[15] sampling gaseous formaldehyde standards generated using a trioxane permeation tube.[22] The agreement between the two monitors, and between the monitors and the standard, is good, particularly considering the difficulty in preparing gaseous HCHO standards at low ppbv levels. A second comparison is shown in Table 2, which lists measurement results for HCHO

**Table 1.** Comparison of Results on Gaseous HCHO Generated by Trioxane Permeation Tube.

| | *Measured HCHO, ppbv* | |
|---|---|---|
| *Prepared HCHO,[a] ppbv* | *Pararosaniline Monitor* | *UV-Fluorescence Monitor* |
| 12.3 | 7.0 | 9.0 |
| 24.7 | 21.6 | 20.9 |
| 49.3 | 49.5 | 50.1 |

[a]: Based on dilution flows and nominal 260 ng/min rate of trioxane permeation tube.

produced in a smog chamber by UV irradiation of a toluene/NO/$NO_2$ mixture.[22] Measurements were made under various chamber conditions on five test days during a 2-month period, by the HCHO monitor and by integrated methods using DNPH in impingers and Sep-Pak® cartridges. The continuous real-time data were averaged over the 60- to 150-minute sampling periods required by the DNPH methods. Table 2 shows agreement between the monitor and the DNPH methods that is generally within 15 percent at concentrations of 20 to 100 ppbv.

Another comparison of continuous real-time and DNPH results was conducted using data from the HAPS study.[20] In those measurements, the monitor sampled indoor and outdoor air for alternate half-hour periods (see Field Measurements, below), while DNPH impinger samples were collected outdoors over 3-hour intervals. A comparison of 11 DNPH results to the corresponding averaged continuous data produced the linear regression

$$\text{Real-Time HCHO} = 1.29\ (\pm 0.33)\ [\text{DNPH HCHO}] - 0.04\ (\pm 0.49)\ \text{ppbv}$$

where the error bars are 95 percent confidence limits. The correlation coefficient (r) of these data is 0.79. The agreement in this comparison is good considering that all 11 data points were below 4 ppbv. A single comparison of indoor HCHO levels from the same study showed 35.4 ppbv HCHO by DNPH, and 38.6 ppbv by the continuous monitor.

**Table 2.** Comparison of Results on Gaseous HCHO Produced in Smog Chamber Experiments.

| | *Measured HCHO, ppbv* | | |
|---|---|---|---|
| *Date of Experiment* | *DNPH Impinger* | *DNPH Cartridge* | *UV-Fluorescene Monitor* |
| 1/3/90 | 20.3 | – | 25.3 |
| 1/4/90 | 25.2 | – | 24.8 |
| 1/5/90 | 22.7 | – | 24.2 |
| 2/15/90 | 99.7 | 92.9 | 106.5 |
| 2/15/90 | – | 96.6 | 113.8 |
| 2/16/90 | 38.2 | 43.7 | 48.0 |
| 2/16/90 | – | 45.8 | 49.4 |

### *Transfer of gaseous HCHO*

Tests were conducted to determine the suitability of various tubing materials for transfer of low concentrations of HCHO in air.[20] These tests were of interest because as a small polar species HCHO might exhibit troublesome surface adsorption behavior similar to that observed with $H_2O_2$ and $HNO_3$.[e.g., 26] Six types of 1/4-in. o.d. commercial tubing were tested (polyethylene, polypropylene, polyvinyl chloride (i.e., Tygon®), and PFA-, FEP-, and TFE-Teflon), with 12.5 ppbv HCHO in both dry and humidified (≈ 80 percent R.H.) high purity air. The tests were conducted by imposing a 12.5 ppbv step change in HCHO concentration, either directly at the monitor's inlet or through a clean 12-ft length of the tubing to be tested. With the exception of Tygon, none of the tubing materials caused any change in the absolute signal level or time response to the prepared HCHO concentration, in either dry or humid air. This test could not detect any short-term adsorptive loss of gaseous HCHO occurring on a time scale much shorter than the instrumental time response (i.e., on the order of seconds). However, it does indicate that on the time scales of usual interest for HCHO (i.e., minutes to hours), no adsorptive behavior of concern is observed with a variety of materials. Any of the forms of Teflon seems an appropriate choice for sampling of gaseous HCHO.

Lee *et al.*[26] reported drastic reductions in the efficiency of transfer of $H_2O_2$ through sample lines after only short periods of exposure to ambient air. No comparable effect was seen for HCHO in the field studies described below. Continuous sampling of HCHO through several feet of tubing for periods of up to 2 weeks caused no apparent degradation in the HCHO levels observed, including the observation of pronounced and recurrent diurnal changes in HCHO. This finding further indicates that HCHO is much less subject to troublesome adsorptive behavior than is $H_2O_2$.

### *Field measurements*

Examples of continuous ambient HCHO measurements are shown in Figures 3–6. Figure 3 shows indoor and outdoor HCHO measurements from the HAPS field study. In this study, the wet chemical monitor was housed in a small trailer parked at a residence in Columbus, Ohio; measurements were made from the morning of June 20 to the morning of June 30, 1989. Air was drawn for alternate 30-minute periods from above the roof of the house, or from inside the house. In addition, zero air (UHP, Matheson) was supplied in excess to the monitor for 6 minutes centered on the hour, each hour of the field study. Thus the monitor sampled indoor air for 27 minutes, outdoor air for 27 minutes, and zero air for 6 minutes sequentially. The resulting 27-minute average values are plotted in Figure 3. Note that the indoor air HCHO concentrations greatly exceeded the outdoor concentrations. This was generally the case, and required that the sensitivity of the wet chemical monitor be reduced in order to keep the indoor values onscale, while maintaining enough sensitivity to measure the outdoor values. Indoor values which were still offscale are shown as diamonds in Figure 3. The outdoor data never exceeded 7 ppbv and averaged 3.3 (± 1.5) ppbv over the entire period. The outdoor HCHO concentrations were considerably lower in the final 2 days

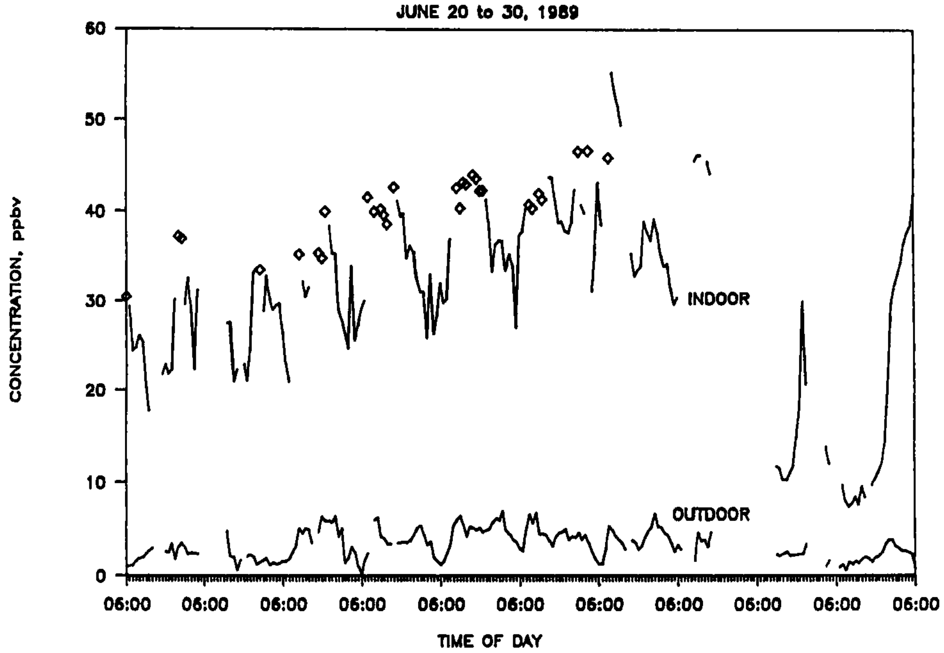

**Figure 3** Continuous indoor and outdoor HCHO data, June 20–30, 1989, Columbus, Ohio. Indoor data which were offscale represent lower limits (◊).

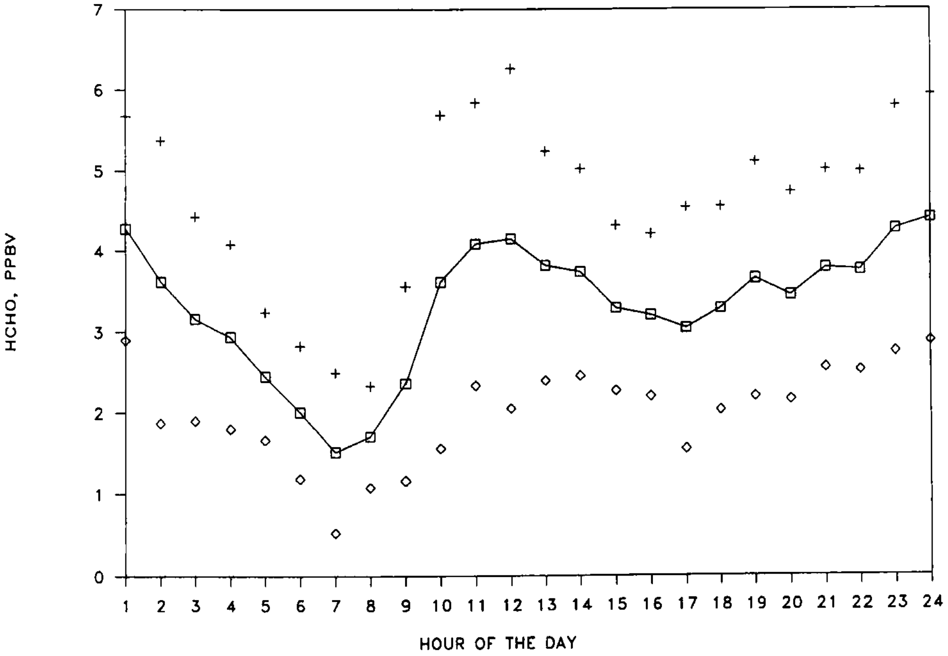

**Figure 4** Diurnal variation in outdoor HCHO found in the continuous monitoring shown in Figure 3. The hourly means (± one standard deviation) are shown.

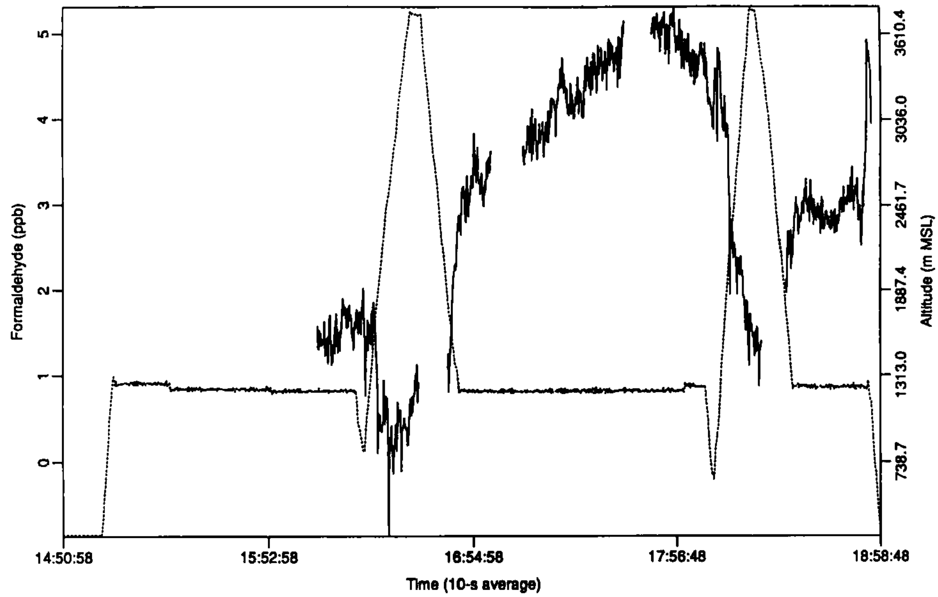

**Figure 5** Continuous airborne HCHO data. HCHO data, solid trace, left axis; aircraft altitude, dotted trace, right axis. Time shown in GMT.

of the study, following passage of a cold front, averaging 2.1 (± 0.8) ppbv. Indoor levels were also lower during most of this period due to increased ventilation of the home. A strong diurnal pattern in the outdoor HCHO was observed, as shown in Figure 4. This figure shows the mean HCHO concentration (± one standard deviation) for each hour of the day, for the June 20–30 period. Minimum average values of about 1.5 ppbv occurred at 7 a.m., and maximum values averaging over 4 ppbv occurred in both late morning and evening. The diurnal profile observed resembles that reported for other urban locations,[10,12,22] and probably results from the interaction of direct emission of HCHO from vehicles, photochemical production of HCHO in the atmosphere, and loss of HCHO to the surface at night.

A second example of low-level continuous HCHO measurements is drawn from use of the monitor aboard Battelle's G-1 aircraft in the Acid-MODES field study.[23] The monitor was flown on the G-1 on 12 flights between May 3 and May 21, 1990. Figure 5 shows the results of one such flight conducted in clear conditions two days after passage of a cold front through the study area. That flight originated and ended in Columbus, Ohio, and covered portions of Kentucky and Ohio. The aircraft remained at altitudes near 1.3 km (relative to mean sea level) for most of the flight, but also conducted two vertical profiles up to 3.8 km altitude, about 500 km and about 2 hours apart, over the southern Kentucky border and over northwest Ohio, respectively. Figure 5 shows both aircraft altitude and HCHO concentration, plotted versus time (GMT), and illustrates that HCHO levels of about 2 to 5 ppbv were observed at the 1.3 km flight altitude. The highest levels were observed during the later portions of the flight, which occurred during early afternoon. Both vertical profiles indicate

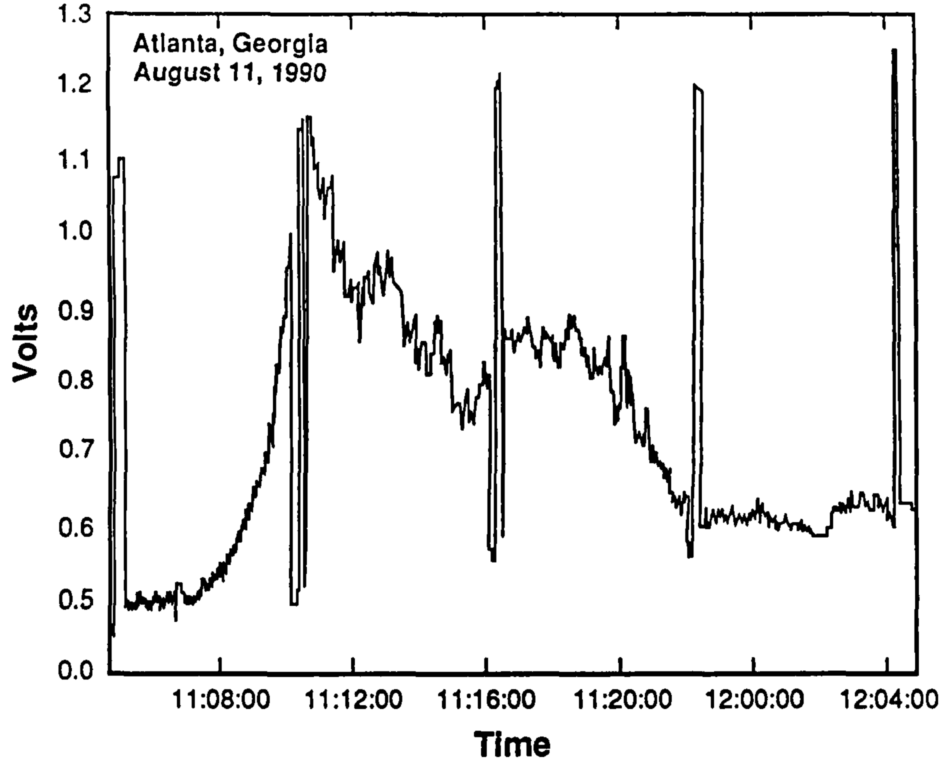

Figure 6 Continuous HCHO data from Atlanta Ozone Precursor Study, August 11, 1990. Automatic zero and span intervals are shown. Time indication is dd:hh:mm.

HCHO levels dropping off sharply at altitudes above about 1.5 km. Thus HCHO shows a vertical profile that resembles those found for oxides of nitrogen ($NO_x$), $SO_2$, and aerosol particles, pollutants known to originate primarily from sources near the surface. Other flights in the study showed similar HCHO levels in clear air, and similar vertical profiles. However, levels consistently below 1 ppbv were observed on all flights conducted in rainy situations, suggesting physical scavenging and/or reduced photochemical formation of HCHO under such conditions.

A final example of continuous HCHO measurements is from the Atlanta OPS, where the monitor was used for 2 weeks in August 1990 at a ground site in South Dekalb, Georgia.[22] Figure 6 shows an example of one day's raw data from the OPS study. The automated zero and span intervals are clearly evident in the figure, as is a pronounced diurnal variation in ambient HCHO. The ambient data showed HCHO levels consistently less than 0.2 ppbv between about 10 p.m. and 6 a.m. each day, with daytime values up to 13 ppbv and averaging about 4 ppbv. During precipitation events daytime HCHO concentrations were reduced, and lower concentrations were observed on cool, cloudy days than on hot hazy days. Daily maximum concentrations usually occurred around midday, with frequently a secondary maximum in the evening. This pattern is similar to that observed in the HAPS field data, noted above.

The usefulness of the monitor in field applications is illustrated by the data shown in Figures 3–6, but examples from other applications could also be given.[21] The monitor was used to test the efficiency of adsorbent media, intended for air purification in the National Archives II building under construction in College Park, Maryland. In that test the target downstream level was 4 ppbv, however, the monitor provided measurements showing that downstream levels never exceeded 0.4 ppbv, indicating that the adsorbent media not only met but exceeded the study requirements. The monitor has also been used in several applications requiring measurement of elevated (i.e., ppmv) levels of HCHO,[20] by reducing the sensitivity of the fluorometric measurement. Examples of such studies include chamber tests of HCHO emissions from construction materials and from gas burners, and confirmation of prepared HCHO levels in chambers during product exposure tests.

The continuous HCHO monitor described here provides a unique combination of desirable characteristics. The Hantzsch reaction provides a highly selective derivatization of gaseous HCHO with simple, inexpensive, and stable reagents. Excitation at 254 nm optimizes the sensitivity of the fluorescence detection of DDL. The resulting fluorescence sensitivity is sufficient to produce a 0.2 ppbv limit of detection with the glass coil scrubber, despite the relatively low air/water contact ratio of the glass coil. This detection limit is comparable to those of the most sensitive previous HCHO monitors. In essence, the improved fluorescence sensitivity is used to compensate for the relatively limited concentrating effect of the glass coil scrubber, thereby taking advantage of the coil's other valuable characteristics. The glass coil provides the characteristics of high efficiency of collection, stability of behavior, ruggedness, and simplicity of design to a greater extent than other scrubber designs, resulting in a sensitive but also highly reliable monitor. The monitor also provides time response superior to that of previous HCHO monitors, a key characteristic for continuous real-time monitoring. It should be noted that the increased sensitivity arising from excitation at 254 nm is a consequence of the high intensity of the light source and the strength of absorption by DDL. Development of an alternative higher intensity source adaptable to portable continuous monitoring (i.e., a small, inexpensive laser emitting at either 254 nm or 410 nm) would likely provide even higher sensitivity.

A potential limitation of the present device is the deposition of aerosol particles in the glass coil scrubber. In tests of particle transmission through a variety of scrubber designs, Genfa *et al.*[19] showed losses of sub-micron particles of up to roughly 50 percent in a glass coil at air flow rates similar to those used here. However, Genfa *et al.* used worst-case test conditions, employing polymer or silver aerosols under dry conditions which favored electrostatic losses of the aerosols. As a result, it is not clear what relevance those data have for sampling of gaseous HCHO. In the atmosphere, the great majority of HCHO present is expected to be in the gas phase, and deposition of a fraction of the aerosol should have minimal effect on the measured formaldehyde level. Furthermore, ambient measurements with the glass coil indicate little if any effect from collected aerosol. The comparison of ambient HCHO measurements by real-time and DNPH methods in the HAPS study (see above) is one example. Another is the performance of the enzyme-based HCHO monitor, employing the glass coil scrubber, in an intercomparison of HCHO methods in southern

California.[12] Genfa *et al.*[19] also note that field measurements of gaseous $NH_3$ and aerosol $NH_4^+$ indicate low and variable deposition efficiencies for aerosol $NH_4^+$ in the glass coil. It should also be noted that, unlike membrane-based diffusion scrubbers, the efficiency of the glass coil for collection of gaseous HCHO should be unaffected by deposition of a fraction of atmospheric aerosol. In light of the predominance of gaseous HCHO in the atmosphere, we conclude that the potential effect of particle deposition in the glass coil on outdoor gaseous HCHO measurements should be negligible. Similar arguments apply to measurements in indoor air and of emissions into clean air in chamber tests. However, should the glass coil be used in an unusual environment in which a substantial fraction of the HCHO is present in the aerosol phase, the glass coil would provide a HCHO measurement intermediate between the gaseous and total HCHO levels.

## *Acknowledgements*

The assistance of Gerald F. Ward in operation of the monitor is gratefully acknowledged. We also acknowledge the support and encouragement of W. A. McClenny, and helpful discussions and correspondence with R. H. Barnes and P. K. Dasgupta.

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## *Credit*

The development of the HCHO monitor was supported by the U.S. Environmental Protection Agency through Contract No. 68-02-4127. The HAPS study was supported by U.S. EPA, Contract No. 68-D8-0082. Battelle's conduct of the Acid-MODES aircraft study was supported by U.S. EPA, through a subcontract from ENSR Consulting and Engineering, Contract No. 88041. The HCHO measurements in the Acid-MODES study were supported by the Electric Power Research Institute (see reference 22). The evaluation and field testing of the monitor by ManTech were conducted under U.S. EPA support, Contracts 68-02-4444 and 68-DO-0106. Although much of the research described in this paper was funded by the U.S. EPA, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.