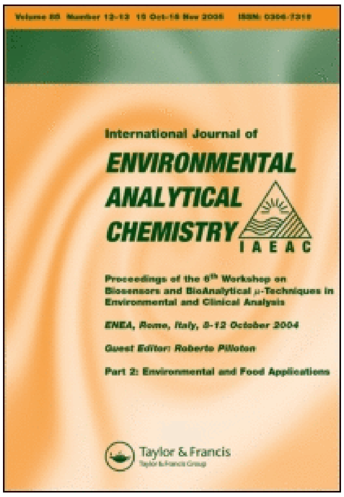

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MEASUREMENT OF ATMOSPHERIC FORMALDEHYDE USING A DROP COLLECTOR AND IN-SITU COLORIMETRY

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A sensitive and affordable approach is described for the *in-situ* measurement of ambient formaldehyde. Air is sampled around a 100 microliter aqueous drop containing 3-methyl-2-benzothiazoline hydrazone. After a desired period of sampling (typ. 5 min) and a waiting period of 10 min for the reaction to be completed, a second reagent ($FeCl_3$) is added to the drop by means of a conjoined conduit. A blue product is formed and is read after an additional 10 min of reaction by a fiber-optic/light emitting diode based photodetector. A fresh drop is then formed and the process begins anew. As demonstrated here, the limit of detection is ~6.25 µg m^{-3} HCHO but can be significantly improved by using longer sampling times and a sampling rate higher than 100 ml min^{-1} used in most of this work. This is the first example of a chromogenic drop sensor that utilizes sequential reagent addition.

Keywords: Formaldehyde; colorimetry; drop sensor; light emitting diode

INTRODUCTION

In recent years, we have been fascinated by the utility of small liquid drops and thin films for sampling in biphasic systems, such as collection of a gaseous analyte or solvent extraction, the analysis being carried out either *in-situ* or *on-line*.[1–8] Ammonia has been collected into a drop of dilute H_2SO_4, withdrawn into a capillary format sequential analysis system and colorimetrically determined.[2] Nitrogen dioxide at ambient levels has been collected into a hanging drop/film of Griess-Saltzman reagent and the resulting purple dye quanti-

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*Corresponding author. Fax: +1-806-742-1289. E-mail: veppd@ttacs.ttu.edu tated by *in-situ* fiber optic/light emitting diode (FO /LED) based colorimetry.[2] Traces of chlorine have been similarly measured, except using continuously forming/falling drops containing the chromogen tetramethylbenzidine.[4] Films supported on a loop have been used to collect a variety of inorganic and organic gases and vapors that are then separated by capillary electrophoresis and quantitated by UV[7] or suppressed conductometric detection.[3] Direct electrochemical sensing of hydroperoxides after collection in a thin film has also been shown to be effective.[8]

In atmospheric analysis, it is frequently important to discriminate between gases and particles because the same analyte can occur in both phases. Diffusion based discrimination is widely practiced to separately collect gases and particles.[9] Drops or films allow:[10] (i) a novel, indefinitely renewable, collection mechanism for analytical purposes (indeed such a mechanism routinely operates in nature as evidenced by the atmospheric cleansing effect of rain), (ii) facile coupling to inexpensive detection systems and (iii) intrinsic discrimination against the collection of particles due to “diffusiophoresis”.[11]

Formaldehyde is the most abundant gas phase carbonyl compound in the ambient atmosphere, ranging in concentration from 10–100 $\mu g\ m^{-3}$ in polluted urban air. It originates both from combustion sources and atmospheric oxidation of hydrocarbons.[12] The measurement of atmospheric formaldehyde has been of considerable interest to us for some time.[13–21] The most sensitive method that we have developed involves the cyclization reaction of formaldehyde collected by a Nafion membrane diffusion scrubber with cyclohexanedione and ammonia;[21] in a recent intercomparison study, this method has compared very well with tunable diode laser spectroscopy.[22]

The present manuscript describes the results of a cooperative effort between Brazilian and U.S. scientists towards the introduction of atmospheric monitoring techniques appropriate to the needs of a developing country. Brazil has a set of unique atmospheric problems because of the widespread use of ethanol as a fuel for internal combustion engines. Partial oxidation of ethanol in vehicular exhaust leads to high levels of acetaldehyde; 60 $\mu g\ m^{-3}$ CH_3CHO and 32 $\mu g\ m^{-3}$ HCHO have been reported in urban air.[23] To our knowledge, there is no other place in the world where CH_3CHO concentrations are so high and exceed that of HCHO. Ethanol for use as fuel is produced by the fermentation of sugar cane juice. Large amounts of sugar cane waste (bagasse) is produced as a byproduct and are typically disposed off by burning. A significant rural and semirural source of HCHO and NO_x is thus created due to biomass combustion. In this context, it is desirable to develop inexpensive means of monitoring NO_x and HCHO and/or other aliphatic aldehydes. These compounds are transported over significant distances and ultimately lead to the photochemically mediated production of peroxyacylnitrates and ozone.[24] With sensitive, affordable and field deployable measurement techniques, these substances can be widely measured in rural areas and the source strengths estimated from multipoint measurements and meteorological vectors. To this end, we have previously designed inexpensive drop-based NO_2 sensors.[2] The fluorometric HCHO instrument[21] is technically suitable but too complex and expensive for the task. Ideally, one should be able to operate such instruments from batteries, this largely rules out fluorometric sensing. Numerous other methods have been described for the determination of atmospheric aliphatic aldehydes in general,[23,25,26] and formaldehyde in particular, by colorimetry.[26] The latter procedures include reactions with chromotropic acid, the Schiff reagent, phenylhydrazine and derivatives and 2-hydrazinobenzothiazoles. The sensitivities for a number of these procedures have been compared[27] and the reaction with 3-methyl-2-benzothiazoline hydrazone (MBTH) was determined to be the most sensitive.[28] In this work, we report a FO/LED-based system that relies on the MBTH chemistry for a portable inexpensive drop sensor that measures HCHO. It is the first sensor to use sequential reagent addition in a drop.

EXPERIMENTAL SECTION

Reagents

All reagents were prepared and stored according to established methods.[29] For the MBTH reagent, a 0.05% solution (2.3 mM) of the hydrochloride salt (Aldrich) was used. One hundred µl was used for each determination. The ferric chloride-sulfamic acid reagent contained 1.6 g sulfamic acid and 1.0 g $FeCl_3$ in 100 mL solution; 40 µl of this reagent was used per determination.

Test Gas Generation

Formaldehyde test gas at $\mu g\ m^{-3}$ concentrations was generated according to Dong and Dasgupta.[15] The experimental arrangement is shown in Figure 1. House compressed air is purified by passage through three sequential columns (A, B, C), respectively containing silica gel washed with concentrated H_2SO_4/$K_2Cr_2O_7$, activated carbon, and 50:50 silica gel/soda lime. One portion of the pure air flow, controlled by needle valve C1 and read by mass flow meter/controller FC1 (model FC-280 or FM-260, Tylan General, Torrance, CA), at 100 ml min^{-1} was directed through a hydrophobic microporous membrane tube E

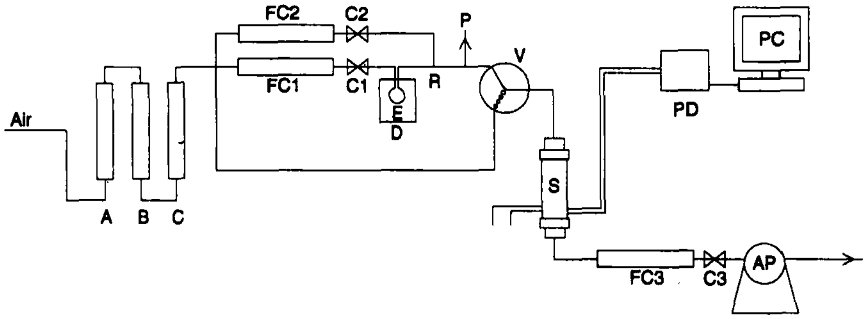

FIGURE 1 Test arrangement. A, B, C: Air purifying columns; C1,2,3/FC1,2,3: needle valve and flow readout, D: Formaldehyde generation source, E: Hydrophobic porous membrane tube immersed in aqueous formaldehyde solution; R tee connection; P: Vent port; V: three way PTFE selector valve; S: Sensor housing, AP: Air sampling pump, PD: photodetector: PC: personal computer based data acquisition system.

immersed in a solution of 2 × 10^{-4} M HCHO in container D. A second flow stream, governed by C2 and FC2, is used for the dilution of the generator output at a tee junction R. Any flow used for sampling is drawn through the three way PTFE solenoid valve V, the remaining is vented through port P. Valve V allows the sampling of either the test gas or pure air through sensor S, the flow through the sensor being governed by flow controller/needle valve C3/FC3 and aspiration pump AP. The sensor has liquid inlet tubes (G, H) and optical fiber connectors that lead to photodetector PD, with the data being acquired and processed by a personal computer PC (*vide infra*).

Sensor Arrangement

The drop sensor S is shown in more detail in Figure 2. It was fabricated from a common chromatography fitting, a 1/4-28 female threaded union U intended for the coupling of two male nuts. Approximately 2–3 mm from the bottom of this union, two adjacent holes are drilled such that two 30 ga. PTFE tubes (Zeus Industrial Products, Raritan, NJ), G and H, can be push fitted into them. At the very bottom edge of the coupling, two 1.5 mm diameter holes are drilled opposite to each other and acrylic optical fibers M and N are push fitted into these. One optical fiber connects to a high brightness (1 cd) 660 nm LED (Stanley Electric, H-1000, Tokyo, Japan) powered at a constant current of 20 mA. The receiver fiber is connected to a photodiode equipped with a 660 nm interference filter (Intor Inc., Soccoro, NM). The light source is referenced by a photodiode

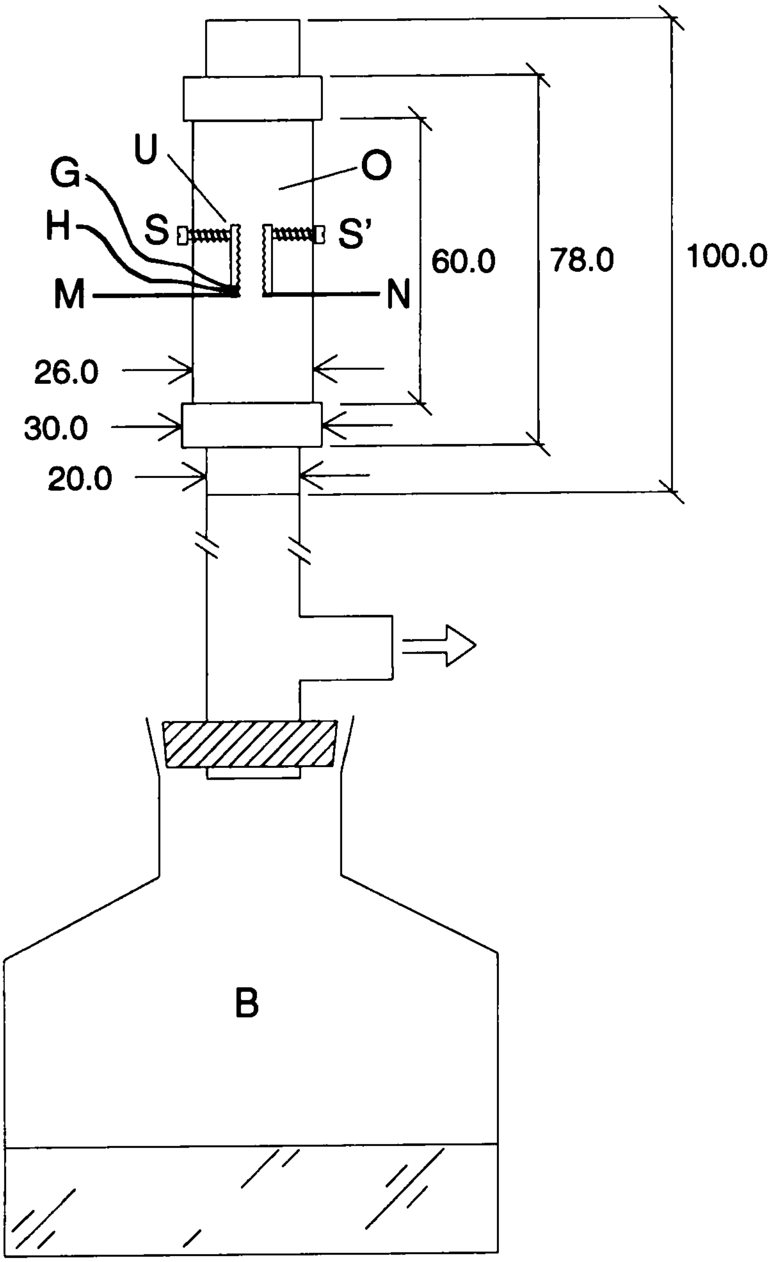

FIGURE 2 Sensor details, dimensions are indicated in millimeters. U: 1/4-28 threaded male-male union, S, S': Screws holding U to sensor outer housing O; G, H: PTFE tubes (connected with dispensing syringes, not shown) connected to U for forming the drop; M, N: Acrylic optical fibers; B: waste bottle.

placed on the backplane of the LED. The reference and signal photodetector outputs are processed by a switched integrator based detector that directly produces the absorbance output,[30] that is acquired by the PC.

The drop sensor housing U is affixed concentrically within an opaque outer tube O, ca. 2.5 cm i.d. and 10 cm long, by means of screws S, S′. The optical fibers and the liquid input tubes exit through the wall of this housing. The outer tube O is provided with caps at each end that have tapered barbs and thus permit facile connection of 1/4-1/2 in. diameter air in/out tubing. Sample gas enters the sensor housing O through the top and is aspirated through the tee junction at the bottom. The sampling rate was 100 ml min^{-1}, except as stated. Liquid waste is collected in the bottle B.

During use, each liquid inlet tube is connected to an 1 ml capacity syringe, each containing one reagent. To obtain a reproducible dispensing of a reagent volume inexpensively, a semi-automated syringe adapter may be used (e.g., Hamilton PB 600); much of the data presented in this paper were, however, generated by careful manual dispensing.

The following experimental protocol was used:

(a) Form an 100 μl droplet of the MBTH reagent (when the amount is dispensed from the syringe, the liquid flows down the threads of the fitting U and forms a hemispheroid drop at the bottom).

(b) Sample the test gas for a fixed time, e.g., 5 min.

(c) Sample pure air for 2 min to flush the sampling zone.

(d) Allow an additional 10 min reaction time for MBTH to react with the collected HCHO.

(e) Add 40 μl of the $FeCl_3$ reagent.

(f) Record the absorbance value after 10 min of adding the $FeCl_3$ reagent as the analytical signal (the color development is not necessarily finished by this time).

(g) Flush out existing liquid with more MBTH reagent, form a new drop and recommence a new sampling cycle (total cycle period is ca. 30 min.)

RESULTS AND DISCUSSION

Initial Considerations

The MBTH reaction was selected for the present work because it permits sensitive colorimetric measurement with relatively simple chemistry. Not only the optimum monitoring wavelength is addressable by an LED, rather bright sources are available in this wavelength region that permits low photometric noise. Although established methods recommend a measurement wavelength of 628 nm,[29] the dye formed absorbs in a very broad spectral region, the half width spanning ~590–700 nm (Figure 3). Since very bright 660 nm LEDs are available commonly and very inexpensively, these were used.

A minor disadvantage of the MBTH chemistry is that it is not selective for HCHO but responds to CH_3CHO as well. However, in emissions from biomass combustion, HCHO emission far exceeds that of CH_3CHO. Additionally, the sensitivity of the MBTH method decreases with decreasing chain length of the aldehyde—at a concentration of 50 $\mu g\ l^{-1}$ in the liquid phase, ethanal and propanal respectively produce an absorbance that is 80% and 58% that of HCHO.[29] Moreover, a liquid drop is a diffusion based collector where collection efficiencies increase with increasing diffusion coefficient and increasing Henry's law solubility (in the solvent constituting the drop).[1] The Graham's law diffusion coefficient of HCHO is 1.21 times that of CH_3CHO and the Henry's law solubility of HCHO[13] is several thousand times greater than that of CH_3CHO.[31]

A more important practical drawback to the MBTH method is that the reaction steps must be sequentially conducted. In the first step, HCHO reacts with MBTH to form an azine. In the second step, the azine is oxidatively coupled to

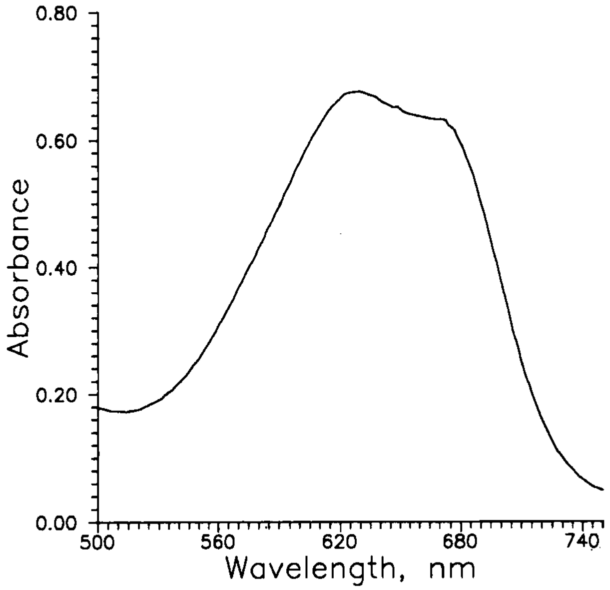

FIGURE 3 Visible spectrum of the analytical reaction product.

a second molecule of protonated MBTH to form an intensely blue cationic dye.[29] The product of analytical interest is not formed if Fe^{3+} is present initially in the MBTH reagent, presumably HCHO is oxidized to HCOOH. The net outcome is that the total sampling and analysis cycle is 30 min long, of this only a relatively small time is actually spent for sample collection. While measurement with this temporal resolution was judged adequate for the present purpose, if a greater temporal resolution is required it is obviously possible to multiplex more than one drop sampler (including the fiber optic) to the sampling pump and detector electronics.

Effects of pH on the First Reaction Step

We studied the effect of the reaction pH in the first reaction step with a view to select best conditions for the determination in terms of both speed and sensitivity. One ml of 25 μM HCHO was added to 10 ml of 2.3 mM MBTH hydrochloride solution, the latter containing additional HCl when it was desired to adjust the reaction pH to less than 5 (the pH obtained without adding additional acid to the reagent). The first reaction step was allowed to occur for periods of 2, 4, 6, 8 and 10 min at three different pH levels (1, 3.5 and 5) following which the $FeCl_3$ reagent (2 ml) was added. Color development was then allowed to continue until the absorbance no longer changed (≤15 min). The results are shown in Figure 4. It is obvious that the reagent without additional acid performs the best and this composition was therefore used. pH values higher than 5 were not investigated: It is difficult to maintain such pH levels because of the absorption of atmospheric CO_2, the concentration of which can be particularly high and variable during biomass combustion events. At an alkaline pH, the reagent is unstable as well.

Brief experiments were conducted with cationic, anionic and nonionic surfactants to determine if they favorably influenced the reaction rate. No particularly attractive results were found.

Signal Profile and Calibration Behavior

Figure 5 shows the temporal development of color after the addition of the $FeCl_3$ reagent. The raw data was acquired with a 1 s time resolution and then smoothed with a 10 point averaging routine using MS Excel. As may be obvious from the data, the initial absorbance is not uniformly zero for the various runs. This minor difference in the starting absorbance is an indication of the scatter and drift inherent with the instrument and the drop measurement technique. In Figure 6, the absorbance after 10 min of reaction is plotted against the HCHO concentra-

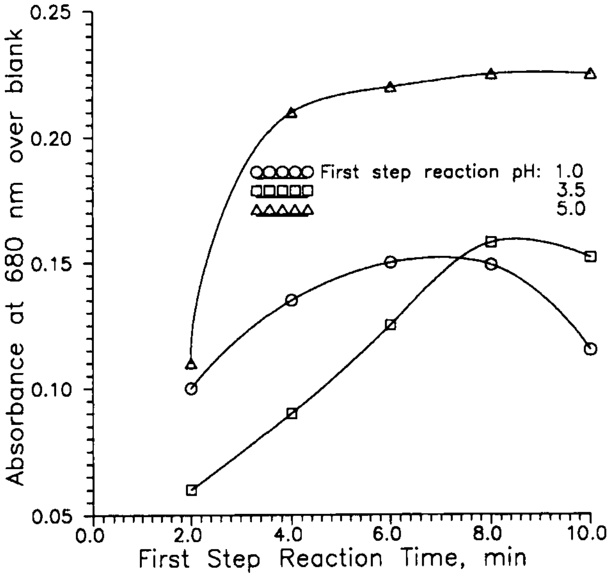

FIGURE 4 Absorbance as a function of the first step reaction time at three different pH levels.

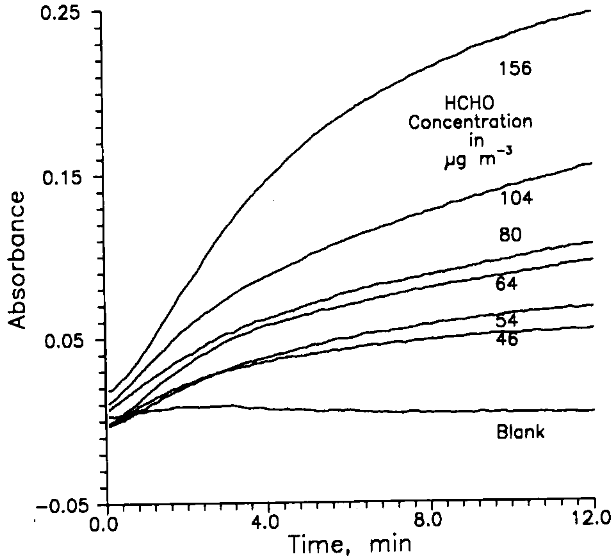

FIGURE 5 The temporal development of color in the second reaction step after various concentrations of gaseous formaldehyde are sampled.

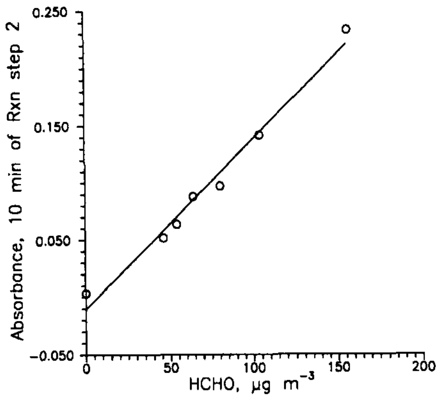

FIGURE 6 Calibration plot for gaseous formaldehyde.

tion sampled. The response is reasonably linear, (r = 0.9916) with a slope of 1.49 mAU/μg m^{-3} HCHO. The detection limit, based on the criteria of three times the standard deviation of the blank is better than 6 μg m^{-3}, adequate for the intended application. However, experiments show that the amount collected increases linearly with time for sampling periods at least up to 30 min and thus the detection limit can obviously be improved by increasing sampling time (as well as by a greater sampling rate, *vide infra*).

It is interesting that in the standard method,[29] the second reaction step is complete within 12 min, at which time the measurement is made. In the present case, the results in Figure 5 make it obvious that the reaction is not complete by this time. This is because the manner of reagent addition as practiced here does not result in rapid mixing. It is possible that a more concentrated $FeCl_3$ reagent solution could be beneficially used to provide an adequate amount of oxidant throughout the drop in a shorter period; note that this reagent does not contribute any significant absorbance background at the measurement wavelength. This was not investigated.

In general, the temporal profile of the color development process fits well to a first order rate process as shown in Figure 7 for the 156 μg m^{-3} formaldehyde sample. This fit predicts an absorbance of 0.28 when the reaction is completed. If it is possible in the field to use a PC to acquire data, it would be possible to compute the best fit ultimate absorbance value and use that as the analytical signal. Such an approach should enhance the signal/noise ratio because it uses the entire temporal profile, rather than the absorbance value at any specific time coordinate.

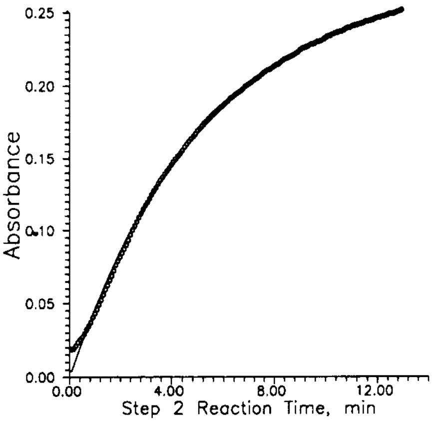

FIGURE 7 The second step color development reaction shows an excellent fit to first order kinetics (circles: experimental data; fit: solid line).

Effect of Sample Flow rate

Figure 8 shows that the response increases significantly with increasing sampling rate. The effect of flow rate has previously been studied for drop samplers, typically the response initially increases almost linearly with increasing flow rate and then tends to reach a plateau;[2,3,8] this is characteristic of a diffusion based sampler.[9] However, this is only true when the collection surface is a perfect sink for the analyte gas. The fact that no indication of a plateau is reached in the present case suggests that surface uptake may be a limiting factor here. At higher flow rates, liquid phase mixing in the drop is enhanced by the frictional drag caused by the air sample moving past the liquid surface, helping to bring fresh MBTH reagent to the surface. Similar effects have been previously observed in other drop collector systems.[1] An altogether different factor may also be operative at higher flow rates. A high sampling rate enhances the evaporation of the drop, resulting in further concentration of the collected analyte. In any case, it is obvious that a considerable further increase in sensitivity may be possible by operating at a flow rate higher than that used in most of this work.

Applications

The instrument was used for sampling both indoor and outdoor air in July and August, 1995. Indoor concentrations in the laboratory were as high as 40 μg m^{-3}, comparable values for our laboratory air have previously been measured by the fluorometric technique.[21] Daytime outdoor concentrations averaged 25 μg m^{-3} similar to values previously measured at this location, with the levels showing a significant decrease after overnight rain.

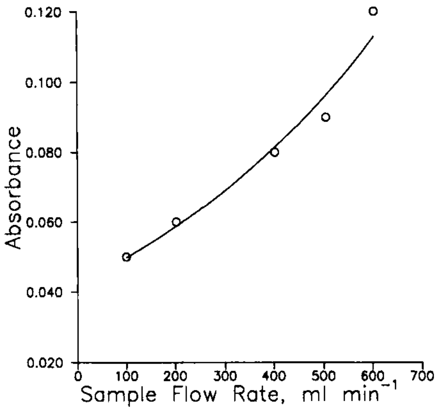

FIGURE 8 Absorbance as a function of air sampling rate (46 μg m^{-3} HCHO, 5 min sample).

CONCLUSIONS

It is felt that we have introduced here a viable and affordable technology for the sensitive measurement of formaldehyde. Indeed, in view of the large number of selective and sensitive chromogenic chemistries that are available in the literature, the basic principle could be applicable in many other cases. Obviously, the actual instrument deployed in the field does not need calibration sources or inlet valves and other test arrangements used in this work. Such calibrations can be conducted in the laboratory. We carried out experiments at a relatively low sampling rate to reduce pumping requirements. However, even modest low power pumps appear to be capable of drawing samples at a rate of 500 ml min^{-1} through the present sensor and should be implemented in the final design along with a hypodermic needle serving as a critical orifice to provide a constant flow rate. For data acquisition, computer requirements are quite limited, even a 80286 class PC is quite acceptable. Such laptop PCs are available rather inexpensively. The use of such a laptop PC suitably equipped with a data acquisition card will greatly enhance the power of the proposed approach.

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References

[1] S. Liu and P. K. Dasgupta, *Anal. Chem.* **67**, 2042-2049 (1995).
[2] A. Cardoso and P. K. Dasgupta, *Anal. Chem.* **67**, 2562-2566 (1995).
[3] S. Kar and P. K. Dasgupta, *Anal. Chem.*, **67**, 3853-3860, (1995).
[4] H. Liu and P. K. Dasgupta, *Anal. Chem.* **67**, 4221–4228 (1995).
[5] H. Liu and P. K. Dasgupta, *Anal. Chem.* **68**, 1817-1821 (1996).
[6] H. Liu and P. K. Dasgupta, *Anal. Chim. Acta.* **326**, 13–22 (1996).
[7] S. Kar and P. K. Dasgupta, *J. Chromatogr.* **739**, 379–387 (1996).
[8] H. Huang and P. K. Dasgupta, *Talanta* (in press).
[9] P. K. Dasgupta, *ACS Adv. Chem. Ser.* **232**, 41–90 (1993).
[10] H. Liu and P. K. Dasgupta, *TrAC*, **15**, 468–475 (1996).
[11] W. C. Hinds, *Aerosol Technology*, (Wiley, New York, 1982). p 161.
[12] Committee on Toxicology and Environmental Health Hazards. National Research Council *Formaldehyde and other Aldehydes* (National Academy Press, Washington, D.C., 1981) 284 pp.
[13] S. Dong and P. K. Dasgupta, *Environ. Sci. Technol.* **20**, 637–640 (1986).
[14] S. Dong and P. K. Dasgupta, *Atmos. Environ.* **20**, 1635-1637 (1986).
[15] S. Dong and P. K. Dasgupta, (1987). *Environ. Sci. Technol.* **21**, 581–588 (1987).
[16] P. K. Dasgupta, S. Dong, H. Hwang, H.-C. Yang and Z. Genfa, *Atmos. Environ.* **22**, 949–963 (1988).
[17] T. E. Kleindienst, P. B. Shepson, C. M. Nero, R. R. Arnts, S. B. Tejada, G. I. MacKay, L. K. Mayne, H. I. Schiff, J. A. Lind, G. L. Kok, A. L. Lazrus, P. K. Dasgupta and S. Dong, *Atmos. Environ.* **22**, 1931-1939.(1988).
[18] P. K. Dasgupta, S. Dong and H. Hwang, *Aerosol Sci. Technol.* **12**, 98–104 (1990).
[19] D. R. Lawson, H. W. Biermann, E. C. Tuazon, A. M. Winer, G. I. Mackay, H. I. Schiff, G. L. Kok, P. K. Dasgupta and K. Fung, *Aerosol Sci. Technol.* **12**, 64–76 (1990).
[20] G. Zhang, P. K. Dasgupta and Y.-S Cheng, *Atmos. Environ.* **25A**, 2717-2729 (1991).
[21] Q. Fan and P. K. Dasgupta, *Anal. Chem.* **66**, 551-556 (1994).
[22] J. G. Calvert, National Center for Atmospheric Research, Boulder, CO, USA. Personal communication (1996).
[23] R. L. Tanner, H. H. Miguel, J. B. Andrade, J. S. Gaffney and G. E. Streit, *Environ. Sci. Technol.* **22**, 1026–1034 (1988).
[24] W. R. Pierson, *Israel J. Chem.* **34**, 335–340 (1994).
[25] A. C. Rayner and C. M. Jephcott, *Anal. Chem.* **33**, 627–630 (1961).
[26] A. P. Altshuller, D. L. Miller and S. F. Sleva, *Anal. Chem.* **33**, 621–625 (1961).
[27] E. Sawicki, T. R. Hauser and S. P. McPherson, *Anal. Chem.* **34**, 1460–1464 (1962).
[28] E. Sawicki, T. R. Hauser, T. W. Stanley. and W. Elbert, *Anal. Chem.* **33**, 93 (1961).
[29] R. J. Bryan, D. L. Hyde, D. A. Levaggi, D. C. Locke, R. A. Rasmussen and P. O. Warner, Methods for Air Sampling and Analysis, 3rd ed., (J. P. Lodge, Jr., ed., Lewis, Chelsea, MI, 1989) pp 279-284.
[30] H. Liu, P. K. Dasgupta and H. J. Zheng, Talanta 40, 1331-1338 (1993).
[31] H. J. Benkelberg, S. Hamm and P. Warneck, *J. Atmos. Chem.* **20**, 17–34 (1995).