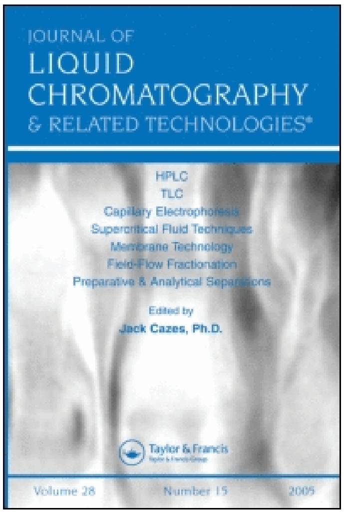
This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Formaldehyde and Other Aldehydes by High Performance Liquid Chromatography with Fluorescence Detection

Stephen J. Swarin[a]; Frank Lipari[b]
[a] Analytical Chemistry Department, General Motors Research Laboratories, Warren, Michigan [b] Environmental Science Department, General Motors Research Laboratories, Warren, Michigan

To cite this Article Swarin, Stephen J. and Lipari, Frank(1983) 'Determination of Formaldehyde and Other Aldehydes by High Performance Liquid Chromatography with Fluorescence Detection', Journal of Liquid Chromatography & Related Technologies, 6: 3, 425 — 444

To link to this Article: DOI: 10.1080/01483918308076059

URL: http://dx.doi.org/10.1080/01483918308076059

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(3), 425-444 (1983)

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH FLUORESCENCE DETECTION

Stephen J. Swarin
Analytical Chemistry Department
Frank Lipari
Environmental Science Department
General Motors Research Laboratories
Warren, Michigan 48090

Downloaded At: 17:48 24 January 2011

ABSTRACT

A sensitive, uncomplicated, and rapid method for the determination of formaldehyde and other aldehydes has been developed. The method is based on the reaction of the aldehyde species with 2-diphenylacetyl-1,3-indandione-1-hydrazone to form fluorescent azine derivatives. The fluorescence excitation and emission spectra have been obtained for several derivatives. The method developed eliminates the lengthy recovery steps required in other methods by performing the sample collection and derivatization directly in midget impingers containing an acetonitrile solution of the reagent. High performance liquid chromatography with fluorescence detection is used to separate and quantitate the individual aldehydes. The detection limits for formaldehyde, acetaldehyde, acrolein, and benzaldehyde are 6 ppb, 4.5 ppb, 0.6 pb, and 0.15 ppb, respectively, in the exhaust gas. The analysis time for the method is about 10 minutes if only one or two aldehydes are of interest. This technique has been used to measure aldehyde emissions from ethanol-, gasoline-, and diesel-fueled vehicles.

INTRODUCTION

Formaldehyde and other aldehydes are a major class of air pollutants produced by many industrial processes and combustion sources. Formaldehyde and many of the other aldehydes have long been recognized as contributors to photochemical smog (1) and

Copyright © 1983 by Marcel Dekker, Inc. 0148-3919/83/0603-0425$3.50/0

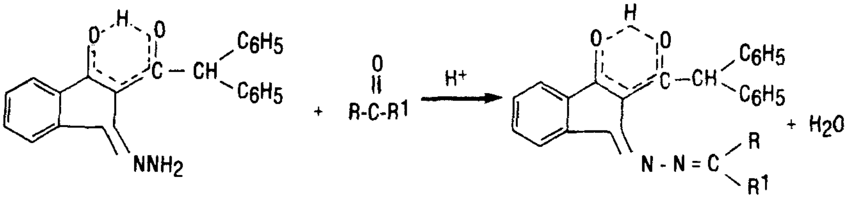
irritants of the skin, eyes, and nasopharyngeal membranes (2). Formaldehyde has been postulated to react with ionic chloride compounds in the air to produce bischloromethylether (3,4), a known carcinogen. Studies conducted at the Chemical Industry Institute of Toxicology (CIIT) indicate an increased incidence of nasal cancers in rats exposed to high formaldehyde levels (15 ppm)(5). The current Occupational Safety and Health Administration (OSHA) 8-hour time weighted average permissible exposure limit for formaldehyde is 3 ppm (6). Lower limits have been recommended by other agencies. Because of the environmental importance of these compounds, a sensitive and rapid technique for their determination in automobile exhaust is needed.

The two commonly used methods of analysis for formaldehyde and other aldehydes in automobile exhaust are the 3-methyl-2-benzothiazolone (MBTH) and the 2,4-dinitrophenylhydrazine (DNPH) methods. The MBTH (7) method is a nonselective colorimetric method for low-molecular-weight aliphatic aldehydes which measures total aldehydes as their formaldehyde equivalents. The method is insensitive to higher molecular weight and unsaturated aldehydes (e.g., acrolein and benzaldehyde) and recently has been shown to be subject to negative SO_2 interference with results commonly about 25 % low (8).

The DNPH method is based on the reaction of the individual aldehydes and ketones with an acidic aqueous solution of the DNPH reagent to form the hydrazones. The derivatives formed are recovered from the aqueous solution by filtration, extraction, evaporation to dryness, and dilution in a solvent suitable for gas chromatographic (GC) (7-12) or high performance liquid chromatographic (HPLC) analysis (12,13). Although this method separates the aldehydes and ketones and quantitates them individually, the extensive sample preparation is quite time consuming, and sample recoveries for various aldehydes range from 60 to 85 %.

Downloaded At: 17:48 24 January 2011

An interesting but much less used reagent for the analysis of formaldehyde and other aldehyde species is 2-diphenylacetyl-1,3-indandione-1-hydrazone. This reagent, which was first used by Braun and Mosher (14), is potentially useful because it forms fluorescent azine derivatives with aldehydes and ketones as shown in Eq. 1:



1

where R and R^1 can be H.

Determinations of individual aldehyde and ketone species using this reagent have been carried out by spectrofluorimetry (14,15), thin-layer chromatography (15), and reverse phase paper chromatography (16).

In this report we present a new method for the determination of formaldehyde and other aldehydes based on the above derivatization reaction followed by high performance liquid chromatography (reverse phase) and fluorescence detection. The collection of the contaminated air sample and the derivatization reaction are performed in a midget impinger containing an acetonitrile solution of the reagent. Injection of an aliquot of the impinger solution allows direct analysis of the azine derivatives without the lengthy and complicated recovery steps involved in the DNPH method. This method will be used to measure aldehyde emissions from ethanol-, gasoline-, and diesel-fueled vehicles, and the results obtained will be compared to those obtained by an improved DNPH method which we have recently reported (17).

Downloaded At: 17:48 24 January 2011

EXPERIMENTAL

Apparatus. A Waters Model 244 Liquid Chromatograph (Waters Associates, Milford, MA) equipped with a Model 440 UV detector (254 nm) and a U6K injection was used. The mobile phase composition was controlled by a Model 1612-B Program Control Module based on a Commodore 2001 Series Microcomputer (Munhall Co., Worthington, OH) A Perkin Elmer MPF-2A fluorescence spectrophotometer equipped with a flow cell (Part No. 63-0576, Perkin-Elmer Corp., Norwalk, CT) was used as a detector and for fluorescence scanning of the derivatives.

Reagents. The mobile phase was made from HPLC grade acetonitrile (Fisher Scientific, Pittsburgh, PA) and deionized water. The 2-diphenylacetyl-1,3-indandione-1-hydrazone was obtained from Aldrich Chemical (Milwaukee, WI) and used as received. All other chemicals and the aldehydes were the best available grade from various suppliers. The chromatographic column was 25 cm x 4.6 mm Zorbax ODS (duPont Instruments, Wilmington, DE).

Confirmation of the Identity of Derivatives. A few milligrams of the azine derivatives of formaldehyde, acetone, acrolein, and benzaldehyde were prepared according to the procedure of Braun and Mosher (14). Their identity was confirmed by high resolution mass spectrometry using a Varian 212 mass spectrometer (Florham Park, NJ). The identity of these derivatives in several LC preparations was confirmed by comparing the retention times to those of these known standards.

Preparation of Solutions and Standards. The absorber solution was prepared as a saturated solution in acetonitrile by adding 100 mg of 2-diphenylacetyl-1,3-indandione-1-hydrazone to 100 mL of acetronitrile with stirring. Just before use the solution was decanted from the excess reagent. The HCl catalyst was added as 5 drops of 1 N HCl per 20 mL of reagent solution.

Standard solutions of the aldehydes were prepared by injecting 5.0 μL of the aldehyde into a septum-sealed vial containing

Downloaded At: 17:48 24 January 2011

5.00 mL of acetonitrile. The concentrations of these solutions were calculated from the densities of the aldehydes or, in the case of formaldehyde, from the concentration of the stock solution as determined by titration (18).

Generation of Standard Aldehyde Vapors. To generate known atmospheres of formaldehyde, a Kin-Tek Model 670 permeation tube system (Texas City, TX) was used with a Kin-Tek certified paraformaldehyde (α-polyoxymethylene) permeation device. The device was heated to 100°C, and helium carrier gas was used to sweep the formaldehyde vapors from the heater chamber to the midget impingers.

To generate known atmospheres of acetaldehyde, acrolein, and benzaldehyde, the method recently given by Graham (19) for the generation of known atmospheres of isocyanates was adapted. The apparatus shown in Fig. 1 was employed. A known amount of a standard aldehyde solution in acetonitrile (10 to 30 μL) was placed in impinger A, and 10 or 20 mL of the absorber solution was placed in impinger B. Room air was then pulled through both impingers at rates varying from 0.5 to 1.5 L/min with a Bendix BDX-55-HD Super Sampler Pump (Bendix Corp., Lewisburg, WV). The sampling time was varied so that a total volume of 20 L of air was pulled through the impingers. During this sampling time, impinger A was heated for 10 to 45 sec. with a heat gun to ensure volatilization of the aldehydes. The aldehydes were swept out of impinger A and trapped in the absorber solution in impinger B. This technique was used for the recovery and precision studies given in this report.

Procedure for Exhaust Sampling. Aldehyde emissions from various vehicles were measured as the test car was driven on a chassis dynamometer through a cold-start, 18-cycle 1972 Federal Test Procedure (FTP) and then through a hot-start, 18-cycle 1972 FTP. The raw exhaust was diluted with room air by a constant volume sampler (CVS). Exhaust samples taken for analysis were

Downloaded At: 17:48 24 January 2011

Downloaded At: 17:48 24 January 2011

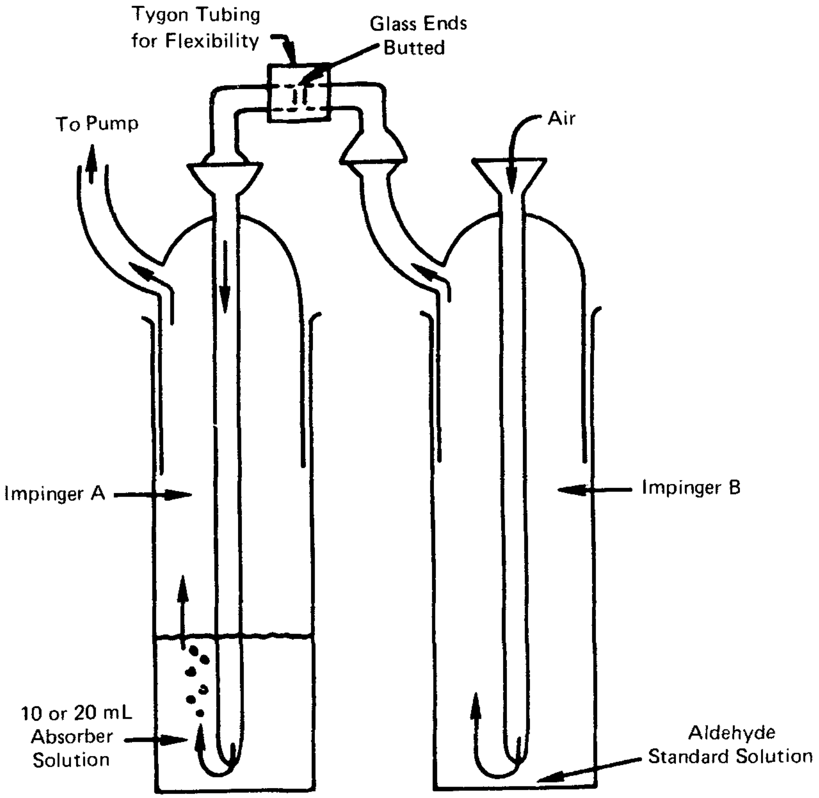


FIGURE 1. Apparatus for generation of known aldehyde vapors.

collected by bubbling the diluted exhaust from the CVS through two midget impingers (Ace Glass, Inc., Vineland, NJ) connected in series. Each impinger contained 20 mL of the absorbing solution. The samples were drawn at a rate of 1.0 L/min by a Dynapump, and the sample volume was measured with a wet-test meter. The CVS sampling line has two sampling ports to facilitate side-by-side sampling and hence alow intercomparison of aldehyde emissions by two analytical techniques.

Downloaded At: 17:48 24 January 2011

RESULTS AND DISCUSSION

Spectral Properties of the Azine Derivatives. Our first step in the development of this method was to prepare mg quantities of a few azine carbonyl derivatives in order to examine their fluorescence spectra. The derivatives were dissolved in acetronitrile and injected into the liquid chromatograph using a mobile phase of 80/20 acetronitrile/water at 2.0 mL/min. Ultraviolet detection at 254 nm was used to determine the elution time so that the flow could be stopped for fluorescence scanning. Figure 2 contains the fluorescence excitation and emission spectra for several azine derivatives and the derivatizing reagent. It can be seen that all of the derivatives fluoresce in a similar wavelength region. The maxium fluorescence emission for all the compounds studied was at 525 nm; the maximum fluorescence excitation varied from 405 nm for the reagent, to 420 nm for the formaldehyde and other aliphatic carbonyl derivatives, to 430 nm for the acrolein derivative, to 440 nm for the benzaldehyde derivative. From this data we chose to use 525 nm as the emission wavelength and 425 nm as the excitation wavelength for fluorescence detection.

Using these wavelengths and 20 nm slits, a study was made of the relative fluorescence intensities of the azine derivatives as a function of concentration. This work showed that unsaturated carbonyl derivatives have fluorescence intensities approximately 2.5 times that of aliphatic carbonyl derivatives. Furthermore, aromatic carbonyl derivatives have fluorescence intensities approximately 8 times that of aliphatic carbonyl derivates. Thus, the detection limits based strictly on fluorescence intensities and diluted standards for the formaldehyde and acetone derivatives are about 50 ng/mL, while those for the acrolein and crotonaldehyde derivatives are about 20 ng/mL, and those for the benzaldehyde and p-tolualdehyde derivatives are about 6 ng/mL. Presumably, this increased fluorescence intensity for unsaturated and

Downloaded At: 17:48 24 January 2011

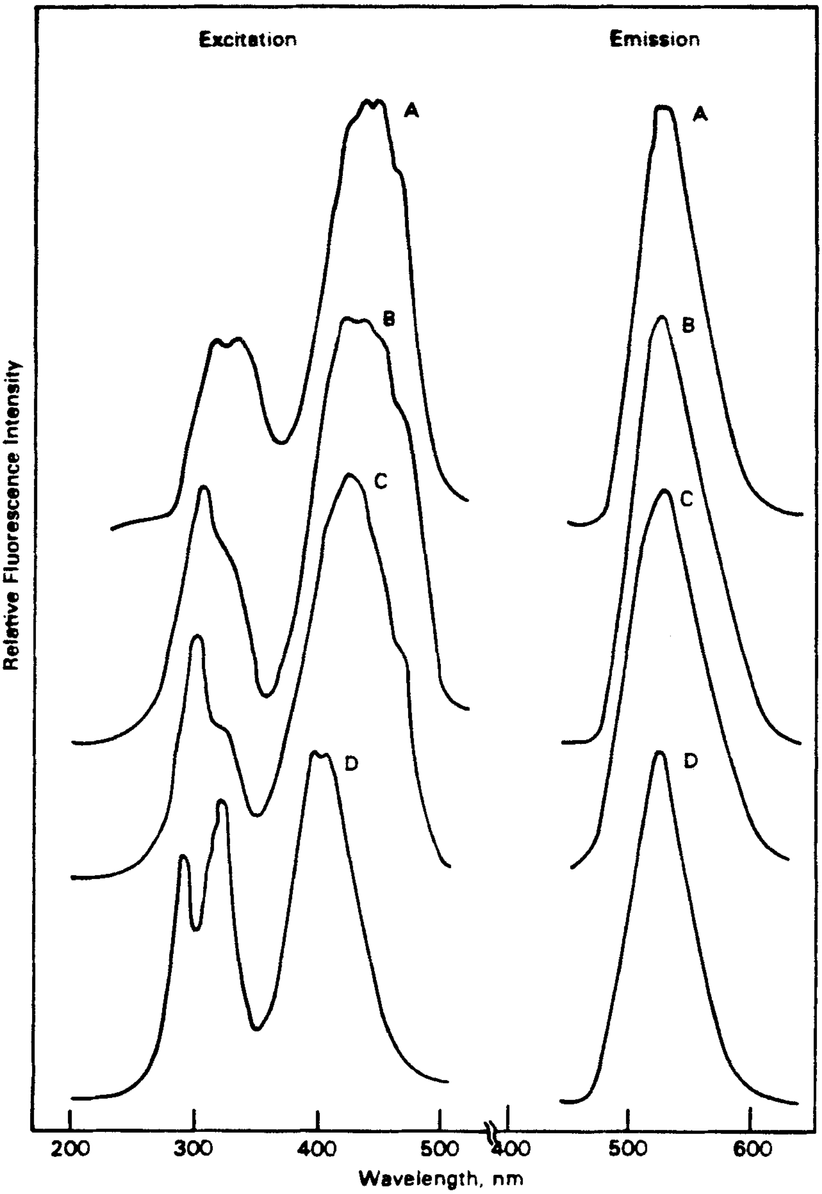


FIGURE 2. Fluorescence spectra of various carbonyl-azine derivatives. 8 nm slits and 25 nm/min scan rate.

A. Benzaldehyde-azine
B. Acrolein-azine
C. Formaldehyde-azine
D. Azine reagent

aromatic carbonyl derivatives is due to the increased conjugation and resonance stability in these derivatives.

Reaction Kinetics of the Derivatization Reaction. The reaction in Eq. 1, to be analytically useful, must proceed rapidly and to completion. Since we hoped to perform both sample collection and derivatization directly in midget impingers, the speed of reaction was critically important. Also, since the concentration of the azine reagent was fixed by its solubility in acetonitrile (0.75 mg/mL = 2.1 μmoles/mL) and since we could not conveniently apply heat to the acetonitrile solution in midget impingers without unacceptable loss of solvent by evaporation, the only reaction variable available for study was the catalyst.

Downloaded At: 17:48 24 January 2011

Pietrzyk and Chan (15) have shown that HCl is the most effective catalyst for this reaction in chloroform solvent; our studies of various mineral and organic acids showed this also to be true in acetonitrile. An extensive study was made of the effect of the concentration of the catalyst. In this study, 0.7 μmole each of formaldehyde, methyl ethyl ketone, and benzaldehyde were injected into 4.0 mL of reagent (8.4 μmoles) containing variable amounts of HCl catalyst (e.g., 1 to 12 drops of 0.5 to 12 N acid). The reaction mixture was then analyzed by reverse phase high performance liquid chromatography (HPLC) at various times after the reaction was begun. The results of this study showed that the reaction was very fast (< 5 min) for the aldehydes at all HCl concentrations. The reaction with MEK was quite dependent on the HCl concentration with > 2 N acid concentrations being required for fast (≤ 10 min) reaction.

These studies also showed that at HCl concentrations greater than 2 N, the ketone-azine derivatives were stable for only about 6 hours. Since our interest was in a fast, simple, and accurate method for formaldehyde and other aldehydes, the optimum HCl concentration was chosen to be 1 drop (50 μL) of 1 N HCl per 4.0 mL of reagent solution. This gives very fast reactions for the aldehydes and fairly fast reactions (≤ 25 min) for the ketones and yields azine-derivative solutions that are stable for at least 8 hours.

High Peformance Liquid Chromatographic Separation of Azine Derivatives. Reverse phase HPLC separation of 15 carbonyl-azine derivatives is illustrated in Fig. 3. Excellent separation is obtained for the important three carbon carbonyls (acetone, acrolein and, propionaldehyde), and very good separation is obtained for the four carbon carbonyls (methyl ethyl ketone, crotonaldehyde, butyraldehyde, and isobutyraldehyde). The resolution of these important three carbon and four carbon carbonyls is superior to any reported for dinitrophenylhydrazine derivatives (12-13,17). We also have attempted to separate the dinitrophenylhydrazine derivatives using various reverse phase columns and find the azine derivatives much easier to separate.

Method Validation. The key feature of the method presented in this report - which makes the determination of formaldehyde and other aldehydes uncomplicated and rapid - is that the collection of the air sample and the derivatization of the aldehydes are performed directly in a midget impinger containing an acetonitrile solution of the reagent and catalyst. This eliminates the lengthy filtration, extraction, evaporation, and dilution steps required in the DNPH methods (9-13). Since the reagent solution in the midget impinger is compatible with the mobile phase in the liquid chromatograph (LC), an aliquot can be withdrawn from the midget impinger (after measuring the final volume in the impinger) and injected into the LC directly. In a study that was published while we were completing our work, Graham used the same approach in a method for the determination of isocyanates (19). He was even able to eliminate the measurement of the final volume of reagent solution in the impinger by adding an internal standard. In the method presented here, the use of an internal standard was not possible because the number of possible aldehydes present in a

Downloaded At: 17:48 24 January 2011

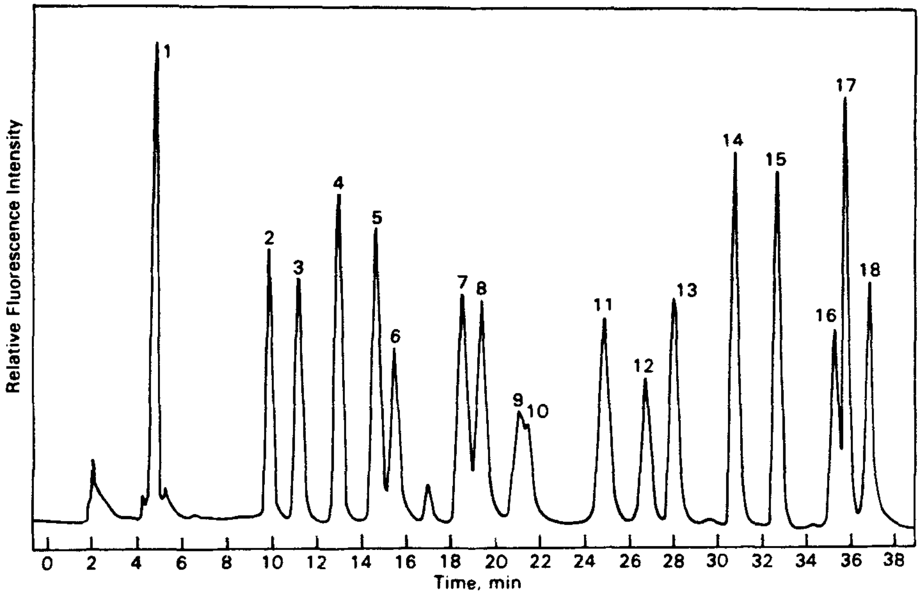


FIGURE 3. Chromatogram of various carbonyl-azine derivatives separated on Zorbax ODS column. Flow rate of 1.0 mL/min; 76 % acetonitrile/24 % water for 18 min, increasing acetonitrile to 100 % over 12 min (2 %/min), and continuing 100 % acetonitrile for 8 min. Fluorescence detection with 20 nm slits and 425 nm excitation and 525 nm emission.

1. Azine reagent
2. Formaldehyde-azine
3. Acetaldehyde-azine
4. Acetone-azine
5. Acrolein-azine
6. Propionaldehyde-azine
7. Methyl ethyl ketone-azine
8. Crotonaldehyde-azine
9. Butyraldehyde-azine
10. Isobutyraldehyde-azine
11. Benzaldehyde-azine
12. Isovaleraldehyde-azine
13. Valeraldehyde-azine
14. p-Tolualdehyde-azine
15. Hexanaldehyde-azine
16. Unknown -from reagent
17. Heptanaldehyde-azine
18. Unknown - from reagent

Downloaded At: 17:48 24 January 2011

sample did not leave sufficient "clear field" in the chromatograms for the internal standard.

In order to determine the collection efficiency of this approach for formaldehyde vapors, we used a paraformaldehyde permeation tube which was found to deliver 2.40 µg/min of formaldehyde by the MBTH method (7). By varying the flow rate of dilution gas over the device from 0.5 to 1.5 L/min, the concentration in the flowing stream was varied between 3.58 and 1.19 ppm. The total sampling time was kept constant at 20 min so that the volume sampled varied from 10 to 30 L while the total formaldehyde generated was constant (48.0 µg). Single midget impingers containing either 10 or 20 mL of absorbing solution were used to collect the formaldehyde vapors. Over this range of sampling conditions we obtained a constant collection efficiency of 98.0 ± 1.5 % (12 determinations).

For the generation of standard atmospheres of other aldehydes, permeation tubes or calibration gas mixtures are not generally available. Therefore a simulated air sampling procedure was devised using the method and apparatus described by Graham (19) (see Experimental). With this procedure, standard 20-L atmospheres of acetaldehyde, acrolein, and benzaldehyde varying from 0.10 to 0.50 ppm were generated. The overall collection efficiency for the method for these aldehydes was 96.0 ± 4.0 % (8 determinations). The precision in this case probably reflects the reproducibility of using a syringe to dispense the dilute aldehyde solutions into the generator impinger.

The detection limits for formaldehyde, acetaldehyde, acrolein, and benzaldehyde were determined and are listed in Table 1. These values are based on three times the noise, or in the case of formaldehyde and acetaldehyde, three times the peak that occurs when an aliquot of the reagent alone is injected. For formaldehyde and acetaldehyde the detection limit would be less

Downloaded At: 17:48 24 January 2011

TABLE 1. Detection Limits for Various Aldehydes

Aldehyde	Detection Limit (v/v) ppb[a]	Detection Limit pg of Aldehyde on Column
Formaldehyde	6[b]	450[b]
Acetaldehyde	4.5[c]	495[c]
Acrolein	0.60	84
Benzaldehyde	0.15	38

[a] Based on a 20-L air sample, a 10-mL final impinger volume, and a 30-μL injection.

[b] A peak equivalent to 2 ppb (150 pg) is encountered in the reagent when no air is sampled.

[c] A peak equivalent to 1.5 ppb (165 pg) is encountered in the reagent when no air is sampled.

Downloaded At: 17:48 24 January 2011

than 1.0 ppb if the blank were zero. A recent paper by Jacobs and Kissinger (20), utilizing the DNPH reagent and electrochemical detection, reports detection limits somewhat lower than these in the case of formaldehyde and acetaldehyde. However these authors utilized only dilution of pure standards to establish their detection limits and did not take into account the possibility of background due to the presence of formaldehyde and acetaldehyde derivatives in the DNPH reagent. Indeed, in our experience the DNPH reagent contains the equivalent of 10 ppb formaldehyde (750 pg) and 5 ppb acetaldehyde (560 pg) even after the reagent has been extensively purified (17). Thus the significant gain in sensitivity claimed by Jacobs and Kissinger would probably not be realized in real samples. The detection limits utilizing the azine reagent and fluorescence detection are superior to any previously reported and reflect the enhanced fluorescence intensities of unsaturated and aromatic carbonyl derivatives discussed earlier. These detection limits could be further improved by purifying the reagent to remove formaldehyde and acetaldehyde derivatives, and by taking larger air samples.

It should be noted that the solubility of the azine reagent in acetonitrile is limited to 0.75 mg/mL which is 42 μmoles in the 20 mL volume used in a midget impinger. We have found that if more than 7 μmoles of formaldehyde are bubbled through a single midget impinger containing this volume of reagent, recoveries of less than 90 % are obtained. Presumably, at a reagent to aldehyde molar ratio of less than 6 to 1 insufficient excess reagent is available to drive the reaction to completion, and some aldehyde escapes the impinger. However, we have also shown that for these high aldehyde samples (7 μmoles of formaldehyde in a 20-L sample is 7.8 ppm), an additional 20 mL of reagent solution contained in a second midget impinger in series with the first will react with an additional 7 μmoles of aldehyde and thus provide additional capacity.

Downloaded At: 17:48 24 January 2011

Stability of the Reagents and Samples. This procedure was developed to give fast turnaround time in emissions testing, so most samples were analyzed within one hour of collection. However, other applications of this technique, such as ambient air monitoring, may require longer time periods between the collection and analysis of samples. In our experience most of the aldehyde derivatives are stable for at least one week only if stored at 0°C; and even under these conditions, only 45 % of the acrolein derivative remains after one week. Recoveries of acrolein of 90 % have been obtained when the 1N HCl catalyst (1 drop per 4.0 mL of reagent solution) is approximately neutralized after collection of the sample by adding 1 drop of 1N NaOH per 4.0 mL of reagent solution followed by storage at 0°C for periods up to one week. However good laboratory practice would dictate that samples be analyzed as soon as possible after collection.

Application of the Method to Auto Exhaust Samples. This method was used to determine the aldehyde emissions from alcohol-, gasoline-, and diesel-fueled vehicles. Diluted

Downloaded At: 17:48 24 January 2011

TABLE 2. Aldehyde Emissions for an Alcohol-Fueled Automobile

Test Cycle[a]	Automotive Catalyst	Aldehyde	Results, ppm in diluted exhaust This Method	 DNPH[b]
Cold Start	No	Formaldehyde	5.93[c]	7.31
		Acetaldehyde	9.32[c]	20.30
Hot Start	No	Formaldehyde	3.43[c]	4.28
		Acetaldehyde	4.54[c]	10.10
40 mph Cruise	No	Formaldehyde	5.86[d]	5.84
		Acetaldehyde	5.00[d]	4.95
Cold Start	Yes	Formaldehyde	0.67[d]	0.71
		Acetaldehyde	19.8[d]	19.9
Hot Start	Yes	Formaldehyde	0.10	0.10
		Acetaldehyde	0.55	0.56
40 mph Cruise	Yes	Formaldehyde	0.36	NA[e]
		Acetaldehyde	0.84	NA

[a] 1972 Federal Test Procedure driving schedule.

[b] Improved DNPH procedure (17).

[c] Emissions exceeded capacity of reagent solution in one midget impinger.

[d] Two midget impingers in series used to increase capacity.

[e] NA - not analyzed.

exhaust (~ 10 to 1) was sampled as outlined in Experimental. Since our dilution tunnel allowed the simultaneous collection of two samples, we were able to collect samples for both the method described in this report and another method to check the accuracy of this method. The independent method used was an improved DNPH method which we have recently reported (17).

Table 2 summarizes the extensive results obtained for a prototype ethanol-fueled automobile. The test cycles refer to 1972 Federal Test Procedure driving schedules. The major aldehyde emissions are formaldehyde and acetaldehyde. Good agreement was

TABLE 3. Aldehyde Emissions for a Gasoline-Fueled Automobile[a]

Test Cycle[b]	Aldehyde	Results, ppm in diluted exhaust	
		This Method	DNPH[e]
Cold Start	Formaldehyde	0.54	NA[f]
	Acetaldehyde	ND (< 0.008)[c]	NA
Hot Start	Formaldehyde	0.097	NA
	Acetaldehyde	ND (< 0.008)	NA
40 mph Cruise	Formaldehyde	0.048[d]	0.052
	Acetaldehyde	ND (< 0.008)	ND (< 0.035)

[a] 1981 Production, Computer Command Controlled, dual-bed catalyst.

[b] 1972 Federal Test Procedure driving schedule.

[c] ND - not detected, detection limit in parenthesis.

[d] Average of 3 determinations, absolute standard deviation = 0.002 ppm.

[e] Improved DNPH procedure (17).

[f] NA - not analyzed.

Downloaded At: 17:48 24 January 2011

obtained between the two methods except in the cases of the cold and hot starts without catalyst where the emissions exceeded the capacity of the azine reagent solution in one midget impinger. Subsequent tests were performed with two midget impingers in series to increase the capacity of the method.

Table 3 shows the results obtained for a gasoline-fueled automobile which contained a 1981 production Computer Command Control exhaust emission system. In this case no acetaldehyde was detected (detection limit = 8 ppb) in the diluted exhaust although low levels of formaldehyde were determined. Again very good agreement was obtained between the two methods. These results also show that very low aldehyde emissions are obtained for these vehicles in contrast to the ethanol-fueled vehicle. The vehicle

TABLE 4. Aldehyde Emissions for a 1978 Diesel-Fueled Automobile[a]

	Results, ppm in diluted exhaust			
	Cold Start[b]		Hot Start[b]	
Aldehyde	This Method	DNPH[c]	This Method	DNPH[c]
Formaldehyde	0.539	0.57	0.428	0.47
Acetaldehyde	0.115	0.13	0.080	0.09
Acrolein	0.057	0.09	0.024	0.09
Propionaldehyde	0.057	0.06	0.024	0.06
Crotonaldehyde	0.011	0.01	0.006	0.01
Butyraldehyde	0.009	0.01	0.008	0.01
Benzaldehyde	0.009	0.01	NA[e]	0.01
Valeraldehyde	0.002	ND (< 0.01)[d]	0.002	ND (< 0.01)
Tolualdehydes[f]	0.001	ND (< 0.01)	0.001	ND (< 0.01)
Total	0.808	0.88	0.573	0.74

[a] 1978 production without exhaust gas recirculation.

[b] 1972 Federal Test Procedure driving schedule.

[c] Improved DNPH method (19).

[d] ND - not detected, detection limit in parenthesis.

[e] NA - not analyzed.

[f] Tolualdehydes are o,m,p-tolualdehydes not resolved under these HPLC conditions.

Downloaded At: 17:48 24 January 2011

test results presented in Tables 2 and 3 show that the method is applicable to aldehyde emissions ranging from 0.05 to 20 ppm.

Table 4 shows results obtained for a diesel-fueled automobile without exhaust gas recirculation. This data demonstrates the number of aldehydes that can be determined in a single test and the wide range in concentration that can be encountered for the individual aldehydes. Considering the low levels of aldehydes involved, generally good agreement was obtained between the two methods, but some loss of chromatographic resolution was observed for the column used for DNPH analysis after 4 months of use and this led to some discrepancies between the two methods (i.e., acrolein in Table 4).

In these tests, where many individual aldehydes were determined, the chromatographic analysis shown in Fig. 3 was used, which led to an analysis time of 45 min per sample including column equilibration. However, in those cases where only a few aldehydes are important or expected, the analysis time can easily be reduced to 10 min per sample.

Downloaded At: 17:48 24 January 2011

CONCLUSIONS

A sensitive, uncomplicated, and rapid method for the determination of formaldehyde and other aldehydes was developed. The method is based upon the collection and derivatization of the aldehydes directly in midget impingers followed by HPLC separation and fluorescence detection of the derivatized aldehydes. The HPLC analysis of an aliquot of the impinger soluion avoids the lengthy recovery steps involved in other methods so that the analysis time may be as short as 10 minutes after sample collection. This technique was used to measure aldehyde emissions from ethanol-, gasoline-, and diesel-fueled vehicles.

ACKNOWLEDGMENT

The authors appreciate the assistance of S. G. Anderson and K. G. Kennedy who operated the emissions facility, and G. N. Nebel who performed the MBTH analyses.

REFERENCES

1. R. A. Bailey, H. M. Clark, J. P. Ferris, S. Krause, and R. L. Strong, "Atmospheric Chemistry," in Chemistry of the Environment, Academic Press, New York, 1978.

2. M. Sittig, "Aldehydes" in Pollution Detection and Monitoring Handbook, Noyes Data Corp., Park Ridge, NJ, 1974.

3. C. C. Yao and G. C. Miller, "Research Study on Bis(Chloromethyl) Ether Formation and Detection in Selected Work Environments," DHEW (NIOSH) Publication No. 79-118, Cincinnati, Ohio, 1979.

4. W. D. Kim, C. L. Geraci, and R. E. Kupel, Am. Ind. Hyg. Assoc. J., 41, 334 (1980).

5. P. Gunby, J. Am. Med. Assoc., 243, (17), 1697 (1980).

6. Title 29, Code of Federal Regulations, section 1910.1001, Table Z-2.

7. M. Katz, Ed., Methods of Air Sampling and Analysis, APHA Intersociety Committee, 2nd Edition, 1977.

8. S. H. Cadle, G. N. Nebel, and R. L. Williams, "Measurement of Unregulated Emissions for General Motors Light-Duty Vehicles," Paper No. 790694, June 12, 1979, Society of Automotive Engineers, Inc., Warrendale, PA 15096.

9. R. A. Smith and I. Drummond, Analyst, 104, 875 (1979).

10. "Procedures for Determining Exhaust Carbonyls as 2,4-Dinitrophenylhydrazones," Final Report in CY 1968 Under CRC APRAC Project No. CAPE-11-68, Fuels Combustion Research Project, Bartlesville Petroleum Research Center, Bureau of Mines, 1969.

11. L. J. Papa and L. P. Turner, J. Chromatog. Sci., 10, 744 (1972).

12. S. Selim, J. Chromatog., 136, 271 (1977).

13. K. Kwata, M. Uebori, and Y. Yamasaki, J. Chromatog. Sci., 17, 264 (1979).

14. R. A. Braun and W. A. Mosher, J. Am. Chem. Soc., 80, 3048 (1958).

15. D. J. Pietrzyk and E. P. Chan, Anal Chem, 42, 37 (1970).

16. R. Brandt, J. C. Kouines, and N. D. Cheronis, Microchem J., 6, 519 (1962).

Downloaded At: 17:48 24 January 2011

17. F. Lipari and S. J. Swarin, J. Chromatog., 247, 297 (1982).

18. "Reagent Chemicals," American Chemical Society, Washington, D.C., p. 274, 1974.

19. J. D. Graham, J. Chromatog. Sci., 18, 384 (1980).

20. W. A. Jacobs and P. T. Kissinger, J. Liq. Chromatog., 5 (4), 669 (1982).

Downloaded At: 17:48 24 January 2011