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DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN AUTOMOBILE EXHAUST WITH AN IMPROVED 2,4-DINITROPHENYL-HYDRAZINE METHOD

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SUMMARY

An improved, simple and rapid method for the determination of formaldehyde and other aldehydes in automobile exhaust was developed. Sample collection and derivatization are performed directly in a midjet impinger containing an acetonitrile solution of 2,4-dinitrophenylhydrazine and catalyst. This scheme eliminates the time-consuming and lengthy recovery steps required in other procedures and allows direct injection of an aliquot of the sample into a high-performance liquid chromatograph for analysis. Detection limits for formaldehyde, acetaldehyde, acrolein and benzaldehyde are 20, 10, 5 and 4 ppb*, respectively, for a 20-l exhaust sample. The analysis time is as short as 10 min if only formaldehyde and acetaldehyde are of interest. The technique was used to measure aldehyde emissions from ethanol-, gasoline- and diesel-fueled vehicles.

INTRODUCTION

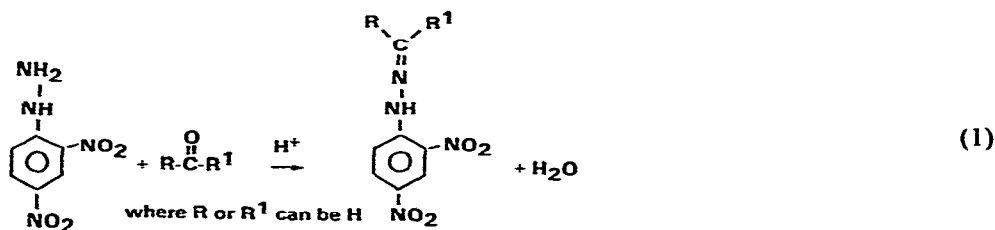
Aldehydes are produced by many industrial processes and combustion sources, including automobile engines. Formaldehyde and many of the other aldehydes are known contributors to photochemical smog¹ and irritants of the skin, eyes and nasopharyngeal membranes². Formaldehyde is postulated to react with ionic chloride compounds in the air to produce bischloromethyl ether^{3,4}, a suspected carcinogen. Studies conducted at the Chemical Industry Institute of Toxicology indicate an increased incidence of nasal cancer in rats exposed to high concentrations (15 ppm) of formaldehyde⁵. The current Occupational Safety and Health Administration (OSHA) 8-h time-weighted average permissible exposure limit for formaldehyde is 3 ppm⁶. Therefore, 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 for the analysis of formaldehyde and other aldehydes in automobile exhaust are the 3-methyl-2-benzothiazolone (MBTH) and the 2,4-dinitrophenylhydrazine (DNPH) methods. The MBTH⁷ method is a non-

* Throughout this article, the American billion (10⁹) is meant.

selective colorimetric method for low-molecular-weight aliphatic aldehydes. This method measures total aldehydes in terms of their formaldehyde equivalents. The method is insensitive to higher molecular weight and unsaturated aldehydes (*e.g.*, acrolein and benzaldehyde) and recently was shown to be subject to a 25% negative interference from sulphur dioxide in automobile exhaust samples⁸.

In the DNPH method, individual aldehydes and ketones react with an acidic solution of DNPH to form hydrazone derivatives as shown in eqn. 1:



These derivatives are removed from the aqueous solution by filtration, extraction, evaporation to dryness, and dilution in a solvent suitable for gas chromatographic (GC)⁹⁻¹¹ or high-performance liquid chromatographic (HPLC)¹²⁻¹⁵ analysis. Although the method separates the aldehydes and ketones and quantitates them individually, the extensive sample preparation is time consuming, and sample recoveries for various aldehydes and ketones range from 60 to 85%.

This paper describes an improved method for the determination of formaldehyde and other aldehydes in which the sample collection and the derivatization reaction are performed directly in a midjet impinger containing an acetonitrile solution of the DNPH reagent. This scheme eliminates the filtration, extraction and transfer steps and allows direct injection of the sample into the HPLC system. During the course of this work, Kuntz *et al.*¹⁶ described a similar procedure. Our report presents further details of this procedure, including collection efficiency studies, breakthrough studies, improved separation of the aldehyde derivatives and defined detection limits. This technique was used to measure aldehyde emissions from ethanol-, gasoline- and diesel-fueled vehicles.

EXPERIMENTAL

Apparatus

All HPLC separations were performed on either a Varian Model 5000 equipped with a 254-nm detector or a Waters Model 244 liquid chromatograph equipped with a Model 440 UV detector. Ultraviolet detection with the Waters instrument was effected at either 254 or 365 nm. Solvent programs were generated via microprocessor control with the Varian instrument and with a Model 1612-B program control module (Munhall Co.) for the Waters instrument. Samples were injected onto the column in the Varian system with a Valco injector and on to the column in the Waters system with a Waters Model U6K injector. The sample sizes injected were 30 μl . Various commercially available reversed-phase (ODS) chromatographic columns

were used to achieve the most efficient separations. These included a 15 cm \times 4.6 mm I.D. Supelcosil LC-18 (Supelco), a 25 cm \times 4.6 mm I.D. Ultrasphere-ODS (Beckman) and a 25 cm \times 4.6 mm I.D. Zorbax-ODS column (DuPont).

Reagents

The mobile phase was prepared from HPLC-grade "distilled in glass" acetonitrile (Fisher Scientific) and deionized water. The 2,4-dinitrophenylhydrazine was obtained from both J. T. Baker and Aldrich. The DNPH was recrystallized from HPLC-grade methanol to reduce carbonyl impurities. All other chemicals and the aldehydes were of the best available grade from various suppliers.

Derivative preparation

The DNPH derivatives were prepared by reacting the corresponding aldehydes with saturated DNPH solution in 2 *N* hydrochloric acid. The DNPH derivatives were filtered, washed with water and 2 *N* hydrochloric acid, air dried and stored in closed vials. Purity was checked by melting-point determinations and by liquid chromatographic analysis. Some of the derivatives were recrystallized from absolute ethanol.

Preparation of solutions and standards

A 6.25 μ mole/ml DNPH stock solution was prepared by addition of 125 mg of purified DNPH crystals to 100 ml of acetonitrile. Dilution of the stock solution with acetonitrile was used to prepare a 3.1 or a 1.6 μ mole/ml DNPH absorbing solution. The catalyst (1 *N* perchloric acid) was added to the absorber solution just before use (1 drop per 5 ml of absorber).

Standard solutions of the aldehydes were prepared by injecting 5.0 μ l of the aldehyde into a septum sealed vial containing 5.0 ml of acetonitrile. The concentrations were calculated from the densities of the aldehydes or, in the case of formaldehyde, from the concentration of the stock solution as determined by titration¹⁷. These solutions were used to generate known atmospheres of aldehydes. Standard derivative solutions were prepared by injecting 2.0–20 μ l of the aldehyde solution into a septum-sealed vial containing the derivatizing reagent and also by weighing the solid hydrazones and dissolving them in acetonitrile.

Generation of standard aldehyde vapors

A Kin-Tek certified paraformaldehyde (α -polyoxymethylene) permeation tube together with a Kin-Tek Model 670 permeation tube system was used to generate known atmospheres of formaldehyde.

To generate known atmospheres of acetaldehyde, acrolein and benzaldehyde, the method described by Graham¹⁸ for the generation of known atmospheres of isocyanates was adapted. The experimental apparatus shown in Fig. 1 was employed. A known amount of an aldehyde solution in acetonitrile (10–30 μ l) was placed in impinger A and 10 or 20 ml of the absorber solution was placed in impinger B. Room air was then drawn 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, U.S.A.). The sampling time was varied so that a total volume of 20 l of air was drawn through the impingers. During this sampling time, impinger A was heated for 10–45 sec with a heat gun to ensure volatilization of the aldehydes. The aldehydes were



Fig. 1. Apparatus for generation of known aldehyde vapors.

swept out of impinger A and trapped in the absorber solution in impinger B. This technique was used for the recovery and precision studies described here.

Procedure for exhaust sampling

Aldehyde emissions from various vehicles were measured as the test cars were driven on a chassis dynamometer. One sample from each test phase was taken from a cold-start, 1-cycle 1972 Federal Test Procedure (FTP) and a hot-start 18-cycle 1972 FTP test. The raw exhaust was diluted with room air by a constant volume sampler (CVS). Exhaust samples taken for analysis were collected by bubbling the diluted exhaust from the CVS through two midget impingers (Ace Glass, Vineland, NJ, U.S.A.) connected in series. Each impinger contained 20 ml of the absorbing DNPH 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.

RESULTS AND DISCUSSION

Reaction kinetics of the derivatization reaction

For the derivatization reaction to be analytically useful, the reaction must proceed in an analogous manner in acetonitrile solvent to that in aqueous solution. A study of the effect of the acid catalyst (hydrochloric and perchloric acids) concentration on the reaction kinetics and derivative stability was undertaken. Known

amounts (0.3–0.5 μmole) of formaldehyde, ethyl methyl ketone and benzaldehyde were injected into 4.0 ml of reagent (6.0 μmole) containing variable amounts of hydrochloric acid catalyst (1–4 drops of 1–12 N acid). The reaction mixture was analyzed by reversed-phase HPLC at various times after the reaction was initiated. The results indicate that the reactions proceed very fast (< 5 min) for the aldehydes at all hydrochloric acid concentrations and that the derivatives are stable for a least 6 h.

The reaction with hydrochloric acid produced a white precipitate, which was later identified by mass spectrometry as 2,4-dinitrophenylhydrazone hydrochloride. A similar study with perchloric acid gave identical reaction kinetics and produced no white precipitate, presumably because of the greater solubility of perchloric acid in acetonitrile. The derivatives were fairly stable (less than 10% decomposition after 24 h with perchloric acid) and subsequently perchloric acid was used in all work.

The optimum reaction conditions chosen were 1 drop (50 μl) of 1 N perchloric acid per 4.0 ml of reagent solution. The concentration of the reagent solution was generally ≤ 6.25 $\mu\text{mole/ml}$, depending on the expected concentration of the aldehydes. At low aldehyde levels where blank impurities become a problem, the concentration of the reagent solution was decreased to 1.56 $\mu\text{mole/ml}$.

High-performance liquid chromatography

An investigation of the resolution obtainable for the DNPH derivatives with three commercially available columns was undertaken (see Experimental). Various mixtures of acetonitrile and water were used as the mobile phases.

The best separation of C_3 aldehyde and ketone derivatives, and indeed the best overall separation, was obtained with a 6- μm Zorbax-ODS column. As can be seen in Fig. 2, the acrolein, acetone and propionaldehyde derivatives are very well resolved whereas the ethyl methyl ketone and butyraldehyde derivatives are not. As acrolein is the more important pollutant, the separations were optimized for the C_3 species at the expense of the C_4 species. This separation scheme was used for most of the automobile exhaust work, as it offered complete resolution of the desired species in a reasonable time. However, with a slightly modified solvent program it is possible to separate even more components (Fig. 3).

Validation of the method

The collection efficiency using the proposed method for formaldehyde vapors was determined using a paraformaldehyde permeation tube. The permeation tube was found to deliver 2.40 $\mu\text{g/min}$ of formaldehyde as determined by the MBTH method⁷. The concentration of formaldehyde was varied from 0.358 to 1.14 ppm by varying the dilution gas (helium) flow-rate of the system from 0.5 to 1.5 l/min. The total sampling time was kept constant at 20 min so that the gas volume sampled varied from 10 to 30 l while the total amount of formaldehyde generated was constant (48.0 μg). The collection efficiency for formaldehyde was $97.5 \pm 1.0\%$ (four determinations) using single midjet impingers containing either 10 or 20 ml of reagent solution.

Atmospheres of other aldehydes were generated using the method and the apparatus described by Graham¹⁸ (see Experimental). Standard 20-l atmospheres of acetaldehyde, acrolein and benzaldehyde with an average concentration varying from 0.10 to 0.50 ppm were generated using this technique. The overall collection efficiency

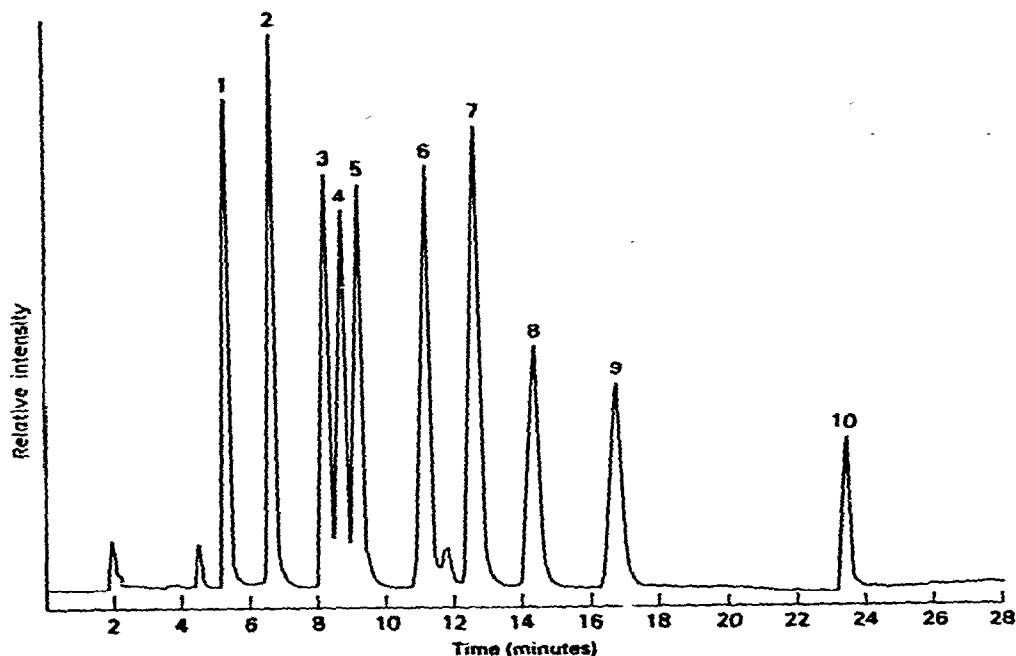


Fig. 2. Chromatogram of various DNPH derivatives separated on a Zorbax-ODS column: acetonitrile-water (65:35) at 1.0 ml/min for 20 min, then gradient to acetonitrile-water (80:20) over 10 min; UV detection at 365 nm. Peaks: 1 = formaldehyde; 2 = acetaldehyde; 3 = acrolein; 4 = acetone; 5 = propionaldehyde; 6 = crotonaldehyde; 7 = ethyl methyl ketone/butyraldehyde; 8 = benzaldehyde; 9 = isovaleraldehyde; 10 = hexanaldehyde.

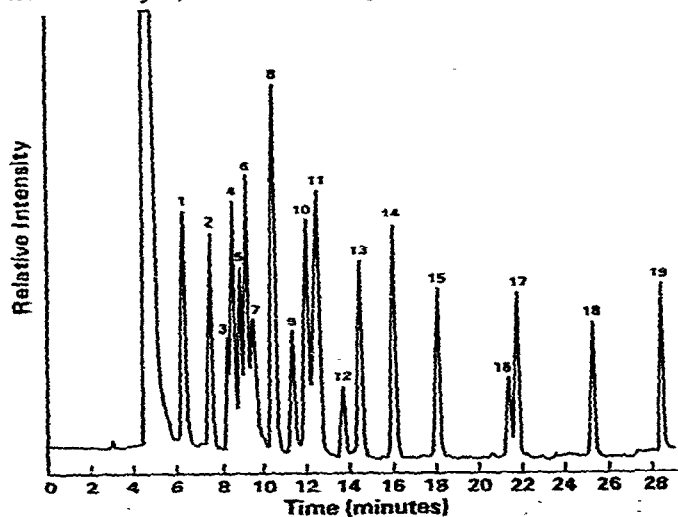


Fig. 3. Chromatogram of various DNPH derivatives separated on a Zorbax-ODS column: acetonitrile-water (67:33) at 0.7 ml/min for 8 min, then 1.0 ml/min and gradient to acetonitrile-water (90:10) over 17 min, then gradient to 100% acetonitrile over 3 min. Peaks: 1 = formaldehyde; 2 = acetaldehyde; 3 = furfural; 4 = acrolein; 5 = acetone; 6 = propionaldehyde; 7 = salicylaldehyde; 8 = crotonaldehyde; 9 = butyraldehyde; 10 = glyoxal; 11 = benzaldehyde; 12 = glutaraldehyde; 13 = valeraldehyde; 14 = *p*-tolualdehyde; 15 = hexanaldehyde; 16 = 3-heptanone; 17 = heptanaldehyde; 18 = octanaldehyde; 19 = nonanaldehyde.

for these aldehydes was $95.0 \pm 4.0\%$ (four determinations each). The precision probably reflects the reproducibility of using a syringe to dispense dilute aldehyde solutions into the generator impinger.

The collection efficiency of this method was compared with the aqueous DNPH procedure¹⁵ by injecting 15- μ l aliquots of dilute solutions of formaldehyde, acrolein, butyraldehyde and benzaldehyde (amounts ranged from 12 to 20 μ g of each aldehyde) into 20 ml of acetonitrile-DNPH and 20 ml of 2 *N* hydrochloric acid-DNPH. The latter solution was extracted three times with pentane and the extracts were combined and evaporated to dryness and the residue was dissolved in 20 ml of acetonitrile. Analysis of the resulting acetonitrile solutions by HPLC allows a direct comparison of the collection efficiency of the two methods, as shown in Table I. The low recoveries and large relative standard deviations shown in this table are probably the result of variable losses during the extraction and evaporation steps required by the aqueous-based procedure. In any event, these collection efficiencies are inadequate for a good analytical method, and they show the superiority of the acetonitrile-DNPH procedure.

TABLE I

COLLECTION EFFICIENCY OF THE 2 *N* HYDROCHLORIC ACID-DNPH PROCEDURE

Efficiency relative to acetonitrile-DNPH procedure.

<i>Aldehyde</i>	<i>Collection efficiency (%)</i> *
Formaldehyde	$86 \pm 10^{**}$
Acrolein	$63 \pm 10; 9 \pm 4^{***}$
Butyraldehyde	80 ± 14
Benzaldehyde	102 ± 7

* Average of at least five determinations.

** Relative standard deviation.

*** The first value is for acrolein alone and the second for acrolein in a mixture with the other three aldehydes.

The detection limits for formaldehyde, acetaldehyde, acrolein and benzaldehyde are listed in Table II. These detection limits are given for UV detection at 365 nm where the DNPH derivatives have their maximum absorbance. Detection at 365 nm as opposed to 254 nm improves the signal-to-noise ratio by a factor of two for

TABLE II

DETECTION LIMITS FOR VARIOUS ALDEHYDES

<i>Aldehyde</i>	<i>Detection limit (ppb, v/v)</i> *
Formaldehyde	20**
Acetaldehyde	10***
Acrolein	5
Benzaldehyde	4

* Based on a 20-l air sample, a 10-ml final impinger volume and a 30- μ l injection.

** A blank peak equivalent to 10 ppb in the reagent based on a 20-l air sample.

*** A blank peak equivalent to 5 ppb in the reagent based on a 20-l air sample.

most of the aldehydes determined and, consequently, improves the detection limit by the same factor. Where no reagent blanks are found (acrolein and benzaldehyde), the detection limits were calculated based on an aldehyde concentration equivalent to twice the noise level. When reagent blank impurity peaks are present (formaldehyde and acetaldehyde), the detection limits are based on an aldehyde concentration equivalent to twice the blank impurity peak. The stock DNPH reagent (6.25 $\mu\text{mole/ml}$) contained 30–40 ppb of formaldehyde equivalents and 15–20 ppb of acetaldehyde equivalents, respectively. Most of the work utilized a 1:4 dilution of the stock reagent, thus reducing the blank impurities. Batch to batch variations in the DNPH reagent can lead to variance in reagent aldehyde impurities and thus affect the detection limits. The detection limit for formaldehyde and acetaldehyde would be about 2.0 ppb if the blank were zero. The detection limits can be improved by further purifying the reagent to remove formaldehyde and acetaldehyde impurities, by taking larger air samples or by increasing the injection volume.

A breakthrough study was carried out to determine the maximum amount of formaldehyde that can be effectively collected in a midget impinger and the point where the collection efficiency deviates from 100%. This study was conducted by bubbling formaldehyde vapor at the rate of 2.4 $\mu\text{g/min}$ into a single midget impinger containing 20 ml (or 31 μmole) of DNPH reagent. The amount of formaldehyde delivered and, hence, the reagent to aldehyde molar ratio was varied by sampling for 20, 60 and 120 min at 1.0 l/min. The resulting molar ratios at these sampling times were 20:1, 6.6:1, and 3.3:1, respectively. Recoveries of $98 \pm 4\%$ were obtained at all three molar ratios tested. Even at a molar ratio of 1.65:1, recoveries in excess of 70% were obtained. Apparently, at a 3.3:1 molar ratio sufficient excess reagent exists to drive the reaction to completion. With 31 μmole of reagent in a midget impinger, 10 μmole of formaldehyde or other aldehyde species can be collected with nearly 100% collection efficiency.

Stability of the reagents and samples

The acetonitrile–DNPH solution is stable for at least 2 months when it is stored at 0°C. However, after the 1 N perchloric acid catalyst has been added, the solution will absorb aldehydes from the air and the catalyst is therefore added just before use.

This procedure was developed to give fast turnaround time in emission testing so most samples were analyzed within 1 h of collection. However, other applications of this technique may require longer time periods between the collection and analysis of samples. In our experience all of the aldehyde derivatives except acrolein are stable in acetonitrile solvent at room temperature for at least 2 weeks. The acrolein derivative decomposes in the presence of excess of DNPH and 1 N perchloric acid at room temperature so that only 30% of the original amount is left after 1 week. Refrigeration at 0°C retards this decomposition significantly so that 85% of the acrolein derivative is left after 1 week. Therefore, refrigeration of samples and standards at 0°C is recommended.

Application of the method to automobile exhaust samples

This method was used to determine aldehyde emissions from ethanol-, gasoline- and diesel-fueled vehicles. The data given in the tables are for diluted exhaust (ca. 10:1) from the CVS system (see Experimental).

Table III summarizes the results obtained for a prototype ethanol-fueled vehicle, a 1974 (no catalyst) gasoline-fueled vehicle and a 1981 (catalyst) gasoline-fueled vehicle. The cold-start and hot-start designations refer to 1972 Federal Test Procedure driving cycles. The major aldehyde emissions found for these vehicles were formaldehyde and acetaldehyde. These vehicle tests show the wide range of concentrations that can be encountered in emission testing and also show that the method developed is applicable to aldehyde emissions ranging from 0.04 to 28 ppm in diluted exhaust. Multiple HPLC analyses of the same sample yielded a reproducibility of $\pm 4.2\%$ (four determinations).

TABLE III

ALDEHYDE EMISSIONS FROM ETHANOL- AND GASOLINE-FUELED VEHICLES

Aldehyde	Results (ppm, v/v) in diluted exhaust					
	Ethanol-fueled*		1974 gasoline-fueled**		1981 gasoline-fueled***	
	Cold start	Hot start	Cold start	Hot start	Cold start	Hot start
Formaldehyde	7.31	4.28	2.42	2.54	0.36	0.04
Acetaldehyde	20.30	10.10	0.67	0.59	0.08	ND
Acrolein	ND	ND	0.27	0.24	0.02	ND
Butyraldehyde	ND	ND	0.03	0.03	0.01	ND
Benzaldehyde	ND	ND	0.10	0.10	0.03	ND
Total	27.61	14.38	3.49	3.50	0.50	0.04

* Prototype 100% ethanol-fueled vehicle.

** No catalyst.

*** Computer command control emission system.

‡ ND denotes not detected (< 0.01 ppm).

TABLE IV

ALDEHYDE EMISSIONS FROM DIESEL-FUELED VEHICLES

Aldehyde	Results (ppm, v/v) in diluted exhaust			
	1978 vehicle*		1980 vehicle**	
	Cold start	Hot start	Cold start	Hot start
Formaldehyde	0.57	0.47	0.70	0.49
Acetaldehyde	0.13	0.09	0.18	0.13
Acrolein	0.09	0.09	0.08	0.05
Propionaldehyde	0.06	0.06	0.05	0.03
Crotonaldehyde	0.01	0.01	0.01	0.01
Butyraldehyde	0.01	0.01	0.06	0.07
Benzaldehyde	0.01	0.01	0.02	0.02
Tolualdehydes	ND***	ND	ND	ND
Total	0.88	0.74	1.10	0.80

* 1978 production vehicle with a 5.7-l, V-8 diesel engine without exhaust gas recirculation.

** 1980 production vehicle with a 5.7-l, V-8 diesel engine with exhaust gas recirculation.

*** ND denotes not detected (<0.01 ppm).

Table IV shows the results obtained for two diesel-fueled automobiles. These data demonstrate the number of aldehydes that can be determined in a single test and the effect of engine configuration on individual aldehyde emissions.

The chromatographic analysis scheme shown in Fig. 2 was used for these tests. With these conditions, an analysis time of about 45 min per sample (including column equilibration) was required. However, when only a few aldehydes are important or expected, the analysis time can be reduced to about 10 min per sample.

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