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Review

Derivatization and chromatographic determination of aldehydes in gaseous and air samples

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Abstract

Various aldehyde derivatives were used for the determination of volatile aldehydes in gaseous or air samples in order to investigate the behaviour of aldehydes in air and their contribution to air pollution. Oxime derivatives of aldehyde are useful for gas chromatographic analysis because the reactions proceed under mild conditions and the derivatives give good separation. Aldehyde pentafluorobenzyloximes are especially superior to aldehyde 2,4-dinitrophenylhydrazones in volatility and sensitivity to GC detection. The technique was applied to the analysis of gaseous and air samples and a method for the determination of volatile aldehydes was developed. This review focuses primarily on the formation of aldehyde oximes, related reactions for GC analysis and other derivatization reactions for GC and HPLC analysis with selective detection.

Contents

1. Introduction

Volatile aldehydes, such as formaldehyde, acetaldehyde, and acrolein, irritate the eyes and respiratory tract. These aldehydes have received attention as hazardous air pollutants. Aldehydes are present in exhaust gases during incomplete burning of organic compounds and are also formed by photochemical reaction with hydrocarbons in air. Aldehydes in air are recognized as contributors to photochemical oxidants that influence human health and plant growth.

Because of the environmental importance of

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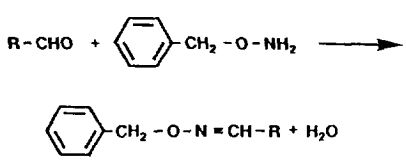
these compounds, sensitive and selective methods for the determination of volatile aldehydes in exhaust gas and/or air are needed. Recently, various derivatization methods and gas chromatographic (GC) and high-performance liquid chromatographic (HPLC) methods for the determination of aldehydes have been reported. Derivatization is very useful in analyses for aldehydes using GC or HPLC with selective detection. This review describes (1) derivatization for sensitive GC analysis, i.e., alkyloxime methods including the pentafluorobenzyloxime method, bromination method with alkyloximes, cysteamine method and oxazolidine method, and (2) derivatization and HPLC methods and applications. We deal here particularly with selective and sensitive chromatographic methods for the determination of volatile aldehydes in gaseous or air samples.

2. Derivatization and gas chromatography

2.1. Oxime derivatization

2,4-Dinitrophenylhydrazone (DNPH) derivatives of aldehydes have been used classically in GC analysis [1–7]. However, the GC analysis of DNPH derivatives needs a high oven temperature because of the low volatility of these compounds. Oxime derivatives of volatile aldehydes show excellent volatility compared with that of DNPH derivatives.

Magin [8,9] reported a qualitative and semiquantitative GC method using benzyloxime derivatives to investigate volatile carbonyl compounds in cigarette whole smoke. The reaction procedure of aldehyde is as follows:



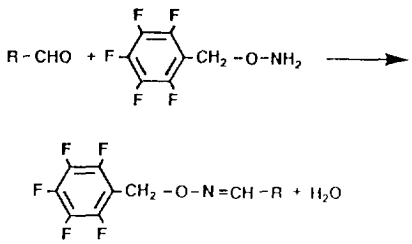
Aldehydes and ketones were trapped on silica gel, eluted with water and derivatilized with benzyloxyamine to form the corresponding oxime. The derivatives were determined by GC with nitrogen-selective detection (NPD). A short free fatty acid phase (FFAP) glass capillary column (12 m) was used for the separation of these compounds. The column oven temperature programme was from 100 to 180°C at 2°C/min. Good separation of many carbonyls was achieved. However, the method is not suitable for the determination of volatile aldehydes because the collection efficiency and detection limit were not reported.

Levine et al. [10] combined several methods to permit the collection, derivatization and determination of low-molecular-mass aldehydes in air samples. The O-benzyloxime derivatization was accomplished by using benzyloxyamine hydrochloride in methanol solution with 0.5 *M* sodium acetate buffer, and was compared with O-methyloxime derivatization as follows:

$$R\text{–}CHO + CH_3\text{–}O\text{–}NH_2 \rightarrow CH_3\text{–}O\text{–}N = CH\text{–}R + H_2O$$

The aldehyde O-benzyloximes were separated by GC. They could be detected with picogram-level sensitivity by NPD. The reaction efficiencies were over 90%. O-Methyloximes of low-molecular-mass aldehydes have high volatility. The technique permits the determination of carbonyls with widely differing volatilities and identification of these compounds from their mass spectra. The detection limit for each aldehyde in air was about 40 ppb (v/v). These methods are adequate for application to automotive exhausts and stationary sources, but not for ambient air measurements.

The O-pentafluorobenzyloxime (PFBO) method is good for the determination of trace levels of volatile aldehydes in air samples. O-Pentafuluorobenzylhydroxylamine (PFBOA) was first synthesized as a derivatization reagent for the GC of keto steroids by Nambara et al. [11]. The reagent was used for carbonyl compounds [12], and was applied to the determination of formaldehyde in clothes [13] and also to the indirect determination of uric acid in serum [14]. The reaction of aldehyde and PFBOA proceeds as follows:



Nishikawa et al. [15] applied the method to the determination of trace amounts of formaldehyde in air. A 1–5-l volume of air was collected in distilled water at a flow rate of 1 l/min. PFBOA solution was added to a portion of the absorption solution and the mixture was allowed to stand for 40 min. Formaldehyde PFBO derivative was extracted with *n*-hexane and determined by GC with electron-capture detection (ECD). Sub-ppb levels of formaldehyde in air could be determined at a sample size of 5 l. The recovery of formaldehyde in air samples was 94% and the calibration graph showed good linearity in the range 10–80 ng in 25 ml of absorption solution. A similar method was reported later by Wolfel et al. [16]. In the analysis of gaseous samples with a complex matrix, such as exhaust gas and emission gas, flame thermionic detection (FTD) or NPD is more effective.

Nishikawa et al. [17] combined a capillary column for the complete separation of aldehydes from ketones and FTD for the sensitive and selective determination of aldehyde PFBO derivatives. As a result, low-molecular-mass aliphatic aldehydes in exhaust gas or thermal degradation emissions could be determined. Aldehydes in sample gas (2–30 l) were collected by passing the gas at a flow-rate of 0.5 l/min through two impingers connected in series. A 10-ml volume of ethanolic PFBOA solution was contained in each impinger. After sampling, the absorption solution was diluted with ethanol and allowed to stand for 80 min. A 10-ml portion of the solution and 20 ml of distilled water were mixed and the mixture was passed through a Sep-Pak C_{18} cartridge. The derivatives in the cartridge were eluted with hexane and determined by GC–FTD. Formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde were determined selectively without interference from ketones. The determination limits were 14 ppb for formaldehyde, 10 ppb for acetaldehyde, 67 ppb for propionaldehyde and 38 ppb for butyraldehyde with 30 l of sample gas. The reaction efficiencies of these aldehydes were over 88% and the collection efficiencies were over 89%.

The PFBO method was applied to the determination of saturated and unsaturated aliphatic aldehydes in environmental water [18], and aldehyde PFBO derivatives were identified by GC–MS. Takino and Yamaguchi [19] reported sample preparation of aldehydes by solid-phase extraction with PFBO derivatization to determine trace amounts of aldehydes in water.

2.2. Bromination of unsaturated aldehyde oxime

Acrolein, a typical unsaturated aldehyde, is an irritant of the skin, eyes and nasopharyngeal membranes. A spectrophotometric method with 4-hexylresorcinol [20] and a fluorimetric method with *m*-aminophenol [21,22] have commonly been used for the determination of acrolein. However, these methods show poor selectivity. Although a GC method based on bromination of acrolein has been reported [23,24], the brominated product of acrolein was unstable and the reproducibility was poor. Nishikawa et al. [25,26] established an improved method based on the bromination of acrolein O-methyloxime to determine trace amounts of acrolein in environmental samples. The reaction procedure is as follows:

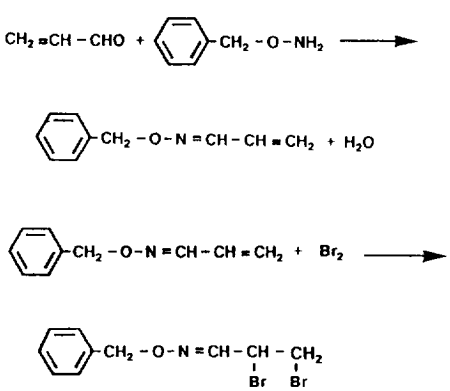
$$CH_2=CH-CHO + CH_3-O-NH_2 \rightarrow CH_3-O-N=CH-CH=CH_2 + H_2O$$

$$CH_3-O-N=CH-CH=CH_2 + Br_2 \rightarrow CH_3-O-N=CH-\underset{Br}{CH}-\underset{Br}{CH_2}$$

The reaction proceeds at room temperature. The reaction product was identified as 2,3-dibromopropionaldehyde O-methyloxime by GC–MS

measurement. The overall reaction efficiency was 92%. The detection limit (signal-to-noise ratio = 2) was 0.4 ng/ml of acrolein in rain water by GC–ECD and the recovery obtained was in the range 90–101%. The method was applied to the determination of acrolein in air samples, i.e., urban air, air in a road tunnel and automobile exhaust [26]. Acrolein in sample gas (3–40 l) was collected at a rate of 0.5–1.0 l/min in two impingers containing ethanol. The collection efficiency was >81%. No interference from co-existing ions, such as chloride, nitrate, nitrite and sulphate ion, was found. The overall detection limit of acrolein in air was about 0.5 ppb with a 40-l air sample.

Another method for the bromination of unsaturated aldehyde oximes was developed. Bromination of the O-benzyloximes was investigated to determine acrolein and crotonaldehyde simultaneously [27]. This method was preferable to the bromination of O-methyloxime derivatives for the determination of acrolein and crotonaldehyde because the reaction efficiency (98% for acrolein and 88% for crotonaldehyde) was higher. The reaction for acrolein proceeds as follows:



The method was applied to the determination of acrolein and crotonaldehyde in automobile exhaust gas, and was suitable for the simultaneous determination of these compounds without any interferences, as shown in Fig. 1. The detection limits were 13 ppb for acrolein and 8 ppb for crotonaldehyde in air samples. The recoveries of these compounds from standard gases were >90% and the relative standard deviations were <5%.

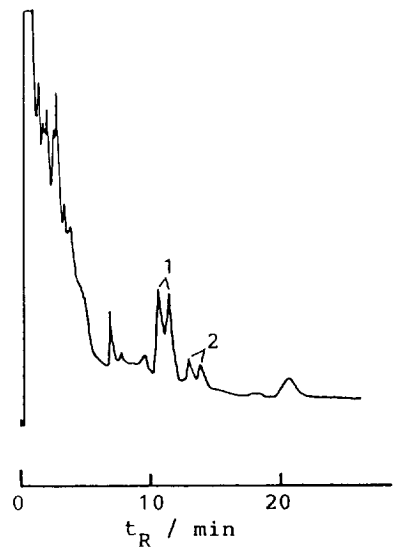


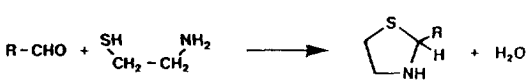
Fig. 1. Typical gas chromatogram of automobile exhaust gas sample. Peaks: 1 = acrolein (*syn/anti* forms); 2 = crotonaldehyde (*syn/anti* forms).

2.3. Other methods

Kennedy and Hill [28] developed a reagent-coated sampling technique for the determination of formaldehyde. Formaldehyde in air reacted with N-benzylethanolamine coated on Chromosorb 102 sorbent to produce 3-benzyloxazolidine. The product was eluted from the sorbent with isooctane determined and by GC–FID. The determination range was 0.55–4.71 mg/m^3 of formaldehyde. The method seems not to be suitable for the determination of formaldehyde in ambient air because the sensitivity was low. A similar approach was demonstrated for acrolein determination [29]. Acrolein in an air sample was collected with 10% 2-(hydroxymethyl)piperidine coated on XAD-2 sorbent to produce 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane. The derivative was eluted from the sorbent with toluene and determined by GC with nitrogen-specific detection. The determination range was 0.13–1.50 mg/m^3 of acrolein. The overall relative standard deviation was 11.1%.

Dimethone derivatives of aldehyde were investigated. Dimedone (5,5-dimethyl-1,3-cyclohexanedione) is a specific reagent for aldehydes [30–32]. Peltonen et al. [33] reported a method for the separation and determination of the dimedone derivatives of aldehyde by capillary GC–ECD. The recoveries of acetaldehyde and *m*-tolualdehyde were >73%. Eight aldehydes were detected in an air sample from thermally degraded epoxy plastic. Acetone, acrolein and propionaldehyde were successfully separated with this method.

Hayashi and co-workers [34,35] developed a method for the determination of formaldehyde and methyl glyoxal in foods and beverages. The method is well known as the cysteamine method. Volatile aliphatic aldehydes react with 2-aminoethanethiol (cysteamine) to form thiazolidine compounds [36]. The reaction proceeds as follows:



The method has the following characteristics, as described by Yasuhara and Shibamoto [36]: only one derivative is formed from one aldehyde; the reaction proceeds rapidly under mild conditions; derivatives can be separated well with a capillary column; and derivatives can be detected selectively with NPD. Yasuhara and Shibamoto reported the physical properties, mass spectra and NMR spectra of thiazolidines [37], and applied the method to the determination of formaldehyde in air samples [38]. The reaction efficiency of formaldehyde with cysteamine was >90.5%. The detection limit was 5.8 pg of formaldehyde and the recovery efficiency of trace gaseous formaldehyde in air was >90%. They reported that the cysteamine method could be used in the range 1 ppb–10 000 ppm of formaldehyde in air and also reported analytical data for aldehydes and ketones in the headspace of heated pork fat [39]. Recently, the cysteamine method was applied to the determination of C_1–C_6 aldehydes in automobile exhaust using GC–NPD by Yasuhara and Shibamoto [40]. The chromatogram showed a good separation of these aldehydes without interferences.

Yasuhara et al. [41] developed a method using N-methylhydrazine to determine acrolein in air. Acrolein reacts with N-methylhydrazine to form 1-methyl-2-pyrazoline. The derivative was determined by GC–NPD. The calibration graph showed good linearity in the range 150 ng–150 μg in 10 ml of dichloromethane. The detection limit was 5.9 pg of acrolein and the recovery efficiency of gaseous acrolein was >98%. The method was applied to the headspace of corn oil and to the exhaust air from a kitchen ventilator [42].

Kashihira et al. [43] reported a simple method for the determination of acrolein in gas samples by GC with chemiluminescent detection. The method is based on the chemiluminescence reaction between ozone and ethylene, which is produced via catalytic decomposition of acrolein on reduced copper in a stream of hydrogen. The determination limit was about 50 ng of acrolein. Acrolein in automobile exhaust could be determined without interference from other hydrocarbons.

3. Derivatization and high-performance liquid chromatography

3.1. DNPH method

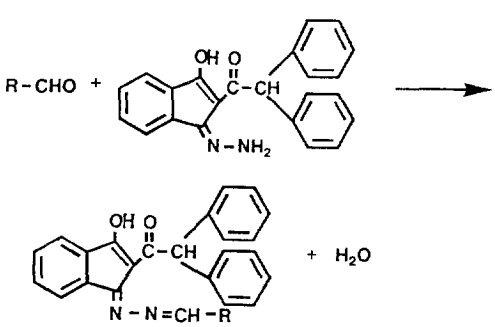
DNPH derivatives of aldehydes are often used in HPLC analyses. The derivatives show strong absorbance of UV radiation. The separation of aldehydes and ketones of identical molecular mass was achieved by HPLC with a reversed-phase μBondapak C_{18} column [44]. One of the sampling techniques for aldehydes in air samples is the impinger method, which uses an absorbing solution containing the reagent 2,4-dinitrophenylhydrazine [45–47]. On the other hand, an absorption column coated with the reagent was used to trap trace levels of aldehydes in air samples. Beasley et al. [48] used a convenient silica column coated with the reagent and hydrochloric acid to determine formaldehyde in air. Grosjean and Fung [49] used a glass cartridge packed with glass beads impregnated with the reagent in phosphoric acid-saturated poly-

(ethylene glycol) to determine volatile aldehydes in air samples. Kuwata et al. [53] applied a Sep-Pak C_{18} cartridge coated with the reagent and phosphoric acid to the determination of C_1–C_4 aliphatic aldehydes in air. The recoveries of the derivatives from the cartridge were >95% and the determination limits were sub-ppb levels of aldehydes for a 100-l air sample. The relative standard deviation was <8.7%. The method may be useful for the routine analysis of air samples.

Lipari and Swarin [51] used a 2,4-dinitrophenylhydrazine-coated Florisil cartridge to determine formaldehyde in air. The determination limit was ppb levels of formaldehyde. Olson and Swarin [52] reported a method for DNPH derivatives of carbonyl compounds by LC–MS. However, in these DNPH methods the reagent blank and contamination from the laboratory atmosphere and water used in analysis must be considered. Karst et al. [53] investigated the interferences of nitrogen dioxide in sampling using a 2,4-dinitrophenylhydrazine-coated solid sorbent. They showed that the products of the nitrogen dioxide–2,4-dinitrophenylhydrazine reaction were 2,4-dinitrophenylazide and 2,4-dinitrochlorobenzene and that only large amounts of nitrogen dioxide would interfere in the determination of formaldehyde.

3.2. Other methods

Swarin and Lipari [54] determined formaldehyde and other aldehydes in automobile exhaust by HPLC with fluorescence detection. The reagent used was 2-diphenylacetyl-1,3-indandione-1-hydrazone, which forms fluorescent derivatives with aldehydes. The reaction proceeds as follows:



The sample collection and derivatization were performed in impingers containing the reagent solution. The mean collection efficiency for aldehydes was 96% and the detection limits were from sub-ppb to ppb levels of aldehydes in the exhaust. Osaki et al. [55] determined acetaldehyde and acrolein in environmental and waste water by HPLC with this reagent. Groemping and Cammann [56] also used this reagent to determine ppb levels of formaldehyde in the atmosphere.

Suzuki [57] reported an HPLC method for the determination of aliphatic aldehydes using cyclohexane-1,3-dione as a fluorescent derivatizing reagent. The determination limit was about 30 pg of each aldehyde. The method was applied to the determination of aldehydes in whisky and it should be applicable to the trace determination of aldehydes in rain water.

Nondek and co-workers [58,59] developed an HPLC technique with fluorescence and chemiluminescence detection using dansylhydrazine [5-(dimethylamino)naphthalene-1-sulfohydrazide]. Sample collection was performed in microcartridges containing porous glass beads coated with the reagent and on-line analysis was used. The detection limits were 0.1 ppb for formaldehyde and acetaldehyde in air. This method was applied to the measurement of sub-ppb levels of aldehydes in a forest atmosphere.

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