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Short communication

Determination of aldehydes in basic medium by gas chromatography using O-benzylhydroxylamine derivatization

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Abstract

The O-benzylhydroxylamine hydrochloride derivatization of aldehydes, like most other aldehyde derivatization procedures, has historically been carried out under acidic conditions. An adaption of this procedure to basic samples, namely triethanolamine, is now reported whereby no acidification of the sample is required. This method has been shown to be capable of quantitatively determining up to at least the C_{10} aldehydes. Analysis by gas chromatography with flame ionization detection gave detection limits in the low μg/ml (ppm) range.

1. Introduction

Ethanolamines are commercially produced by reaction of ethylene oxide with ammonia. The various amines produced are separated by distillation to give monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). While MEA and DEA are usually water white in color, it is not uncommon for TEA to be highly colored. The color-producing impurities have been ascribed to the presence of aldehydes which are either impurities carried into the process with the ethylene oxide or are formed as a result of ethanolamine degradation. In order to study color formation during the production of these amines, it was necessary to have a method capable of determining trace levels of aldehydes in this matrix.

The determination of aldehydes either in total or as individual aldehydes has been described by many investigators. Gas chromatographic (GC) determination of free aldehydes present difficulties due to their reactive nature. Determination using liquid chromatography requires UV detection at 200 to 220 nm and presents a sensitivity issue since extinction coefficients of these aldehydes are not high. An alternative to direct determination is to react aldehydes with a derivatization agent which imparts either thermal stability for GC analysis or a more strongly absorbing chromophore in the UV or visible spectral range for liquid chromatographic analysis.

One of the most common derivatization agents for aldehydes is dinitrophenylhydrazine which when reacted with aldehydes produces a hydrazone product that is both thermally stable and has a strong chromophore. This method has been used for colorimetric [1–3], GC [4–6] and liquid chromatographic [7–9] determinations. This derivatization procedure, however, is an acid-catalyzed reaction which would require

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acidification of a basic triethanolamine matrix. Acidification of this basic matrix could result in heat generation which would, in turn, increase the likelihood of losing the more volatile aldehydes. A second procedure involving the reaction of pentafluorobenzyloxyamine (PFBOA) with carbonyl compounds has been used for trace level detection of aldehydes [10–12]. Samples containing these fluorinated oxime derivatization products have been analyzed by GC with electron-capture detection (ECD). These reactions have been carried out in aqueous solutions and in media which are slightly acidic. A third method which involves formation of aldehyde oxazolidine derivatives is used extensively in air pollution work for screening and determination of various low-molecular-mass aldehydes. The most common reagent is 2-(hydroxymethyl)piperidine which is coated on XAD-2 resin for packing in solid adsorbent tubes [13]. This reagent was found by Kennedy and coworkers [14,15] to give the fastest reaction time for this class of reagents. This derivatization reaction has primarily been used in adsorbent tube reactions for gas-phase reactions rather than for solution-phase derivatizations.

This paper reports on an extension of the PFBOA procedure which demonstrates that the non-fluorinated O-benzylhydroxylamine (BOA) reagent is capable of derivatizing aldehydes in basic media to form aldehyde oxime products which can be quantitatively determined by GC using flame ionization detection (FID). While PFBOA gives good ECD sensitivity, this halogenated derivative decreases the FID response due to quenching of the flame signal by the fluorine. Therefore, the non-fluorinated BOA was chosen to maximize FID sensitivity.

2. Experimental

2.1. Reagents

O-Benzylhydroxylamine hydrochloride (Aldrich, Milwaukee, WI, USA) was prepared as a 5000 μg/ml solution in deionized (DI) water (Millipore, Bedford, MA, USA). Standard solutions (2500 μg/ml) of formaldehyde (Aldrich), acetaldehyde (Aldrich), propanal, butanal, pentanal, hexanal, heptanal (Alltech, Deerfield, IL, USA) were also prepared in DI water. Octanal and decanal standards can also be made in water but only at lower concentrations due to the limited aqueous solubility of these aldehydes. These solutions were diluted with DI water to prepare standards for standard addition and recovery studies. Similar standards were also prepared using TEA as a solvent. Hexane (Burdick & Jackson, Muskegon, MI, USA) was used for extractions.

2.2. Instrumentation

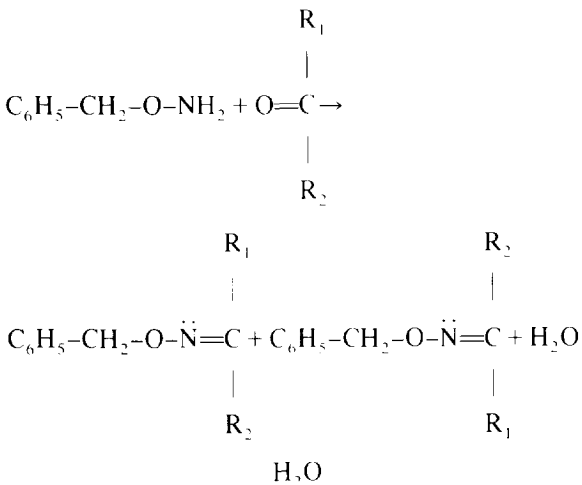
A Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector was used for analysis. A 30 m × 0.25 mm I.D. DB-210 (J & W Scientific, Folsom, CA, USA) fused-silica capillary column (0.25 μm film thickness) was used for GC analysis. Helium was used as the carrier gas at 1.1 ml/min. The column temperature program was 50°C isothermal for 1 min, programmed to 200°C at 6°C min, held for 1 min, ramped again at 25°C/min to 225°C and held for 2 mins. Injection port and detector temperatures were held at 225 and 250°C, respectively.

2.3. Derivatization procedure

A 1-ml volume of sample was accurately weighed into a 4-ml screw-capped vial and 1 ml of the 5000 μg/ml BOA solution was added. The mixed solution was allowed to react at room temperature for 2 h. The derivative product was then extracted in the same vial with 1 ml of *n*-hexane by shaking vigorously for 1 min. The hexane extract was transferred to another vial using a transfer pipet and was shaken well with 4 ml of 0.15 *M* H_2SO_4 for 30 s. This removed excess TEA and BOA from the derivative product. The hexane layer was removed and analyzed for aldehyde content.

3. Results and discussion

BOA reacts with carbonyls (shown below) to form the corresponding oximes. Nonsymmetrical carbonyl compounds ($R_1 \neq R_2$) such as acetaldehyde react with BOA to give two geometrical isomers (based on the position of the R groups relative to the free electron pair of the nitrogen) and two peaks in the chromatogram when a polar column is used. Symmetrical carbonyls ($R_1 = R_2$) such as formaldehyde form a single isomer and give a single peak in the chromatogram. Doublet peaks in the chromatogram of an unknown will therefore give qualitative information regarding the presence of nonsymmetrical carbonyls.



The work presented here shows that this method works effectively for linear straight-chain aldehydes up to at least C_{10} as well as for crotonaldehyde. Fig. 1 shows a standard chromatogram of the C_1–C_{10} aldehyde derivatives and illustrates that formaldehyde gives a single peak while the non-symmetrical aldehydes produce doublets.

The time required to carry out a BOA reaction was studied on TEA samples. A 1-ml volume of a 5000 μg/ml BOA solution was mixed with 1 ml of a TEA solution that had been spiked with known amounts of formaldehyde and acetaldehyde. The high concentration of BOA was used to ensure an excess of BOA. The vials were held at room temperature for periods

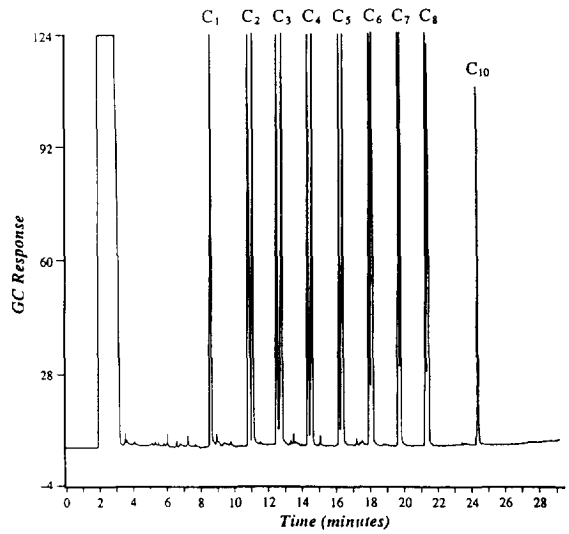


Fig. 1. Gas chromatogram of C_1–C_{10} straight-chain aldehydes using BOA derivatization.

of time ranging from 1 to 36 h. The TEA solutions were then extracted with hexane and analyzed. The results, shown in Fig. 2, indicate that the reaction reached completion in 1.5 to 2 h. The derivatives remained stable for at least 36 h in the TEA–BOA mixture and were also found to be stable in the hexane extract for an equivalent period of time. Since formaldehyde and acetaldehyde are often found in TEA, they were used for optimizing the reaction time. However, crotonaldehyde, hexanal and heptanal were also tested for optimum reaction conditions

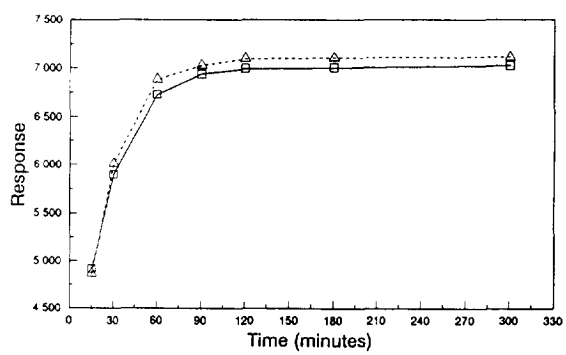


Fig. 2. Plot of flame ionization response versus BOA reaction time. △ = Formaldehyde; □ = acetaldehyde.

and they were found to react quantitatively and within the same time frame.

The derivatization method was confirmed in the TEA matrix by studying the spike recovery. TEA samples were spiked with known amounts (from 20 to 250 μg/ml) of formaldehyde, acetaldehyde, butyraldehyde and crotonaldehyde. The spiked samples were then analyzed using the above procedure and their typical recovery percentages are shown in Table 1. As predicted, two peaks were detected for each non-symmetrical aldehyde with recoveries calculated at greater than 90% for each.

A standard addition method was also used to confirm the concentration of aldehydes in a TEA sample. The concentrations for formaldehyde and acetaldehyde were found to be 18 and 50 μg/ml, respectively, as compared to 19 and 48 μg/ml using an external standard calibration. Since there did not appear to be any matrix effects, the external standard method was used for analyzing TEA samples.

Several TEA samples were then screened for individual aldehydes using the above procedure. Table 2 shows aldehydes found in the various TEA samples with the corresponding color description of the TEA. In all cases, only formaldehyde and acetaldehyde were found. It could not be determined whether formaldehyde and acetaldehyde are responsible for imparting color, however, they correlate with the color in these solutions. Since the method was tested for aldehydes only up to decanal, it could not be determined whether the TEA samples contained aldehydes higher than decanal or if higher-molecular-mass aldehydes were present which either did not elute from the column or which decomposed in the injection port of the chromatograph. At this time, another method [7–9] involving derivatization with dinitrophenylhydrazine was also explored for analyzing aldehydes in TEA samples using HPLC. It was found, however, that the method showed no reproducibility of response for various aldehydes especially formaldehyde and acetaldehyde present in TEA matrix. The non-reproducibility of response

Table 1
Spike recovery results for triethanolamine

Compound	Amount spiked (μg/ml)	Amount recovered (μg/ml)	Recovery (%)
Formaldehyde	20	18	90
	50	52	104
	100	96	96
	150	138	92
	250	235	94
Acetaldehyde	20	19	95
	50	47	94
	100	101	101
	150	140	93
	250	230	92
Butanal	20	18	90
	50	53	106
	100	90	90
	150	142	95
	250	238	95
Crotonaldehyde	20	21	105
	50	46	92
	100	93	93
	150	154	103
	250	228	91

Table 2
Aldehyde analysis in triethanolamine samples

Process sample	Formaldehyde (μg/ml)	Acetaldehyde (μg/ml)	APHA[a] color scale
1	3	24	25
2	6	100	45
3	5	100	55
4	7	110	70
5	7	150	300
6	17	180	500
7	12	260	1500

[a] Official method for color (APHA scale) issued by the American Oil Chemists' Society (AOCS), document no., TD1B, 1964.

could be attributed either to the formation of an unstable hydrazone derivative in TEA or degradation of the hydrazone derivative due to the extreme basic nature of TEA. No other methods were investigated further and the proposed method of BOA derivatization was used for routine aldehyde analysis in TEA.

3.1. Method sensitivity

To verify the linearity of the BOA derivatization method, a calibration for the analysis of formaldehyde, acetaldehyde, butyraldehyde and crotonaldehyde was done over a wide concentration range. The method was found to be linear from the detection limit of 1 μg/ml to approximately 2000 μg/ml with a correlation coefficient of 0.9998. A higher concentration of BOA solution can be used to obtain linearity for samples containing excessive amount of aldehydes. The upper detector linearities of octanal and decanal were 600 and 250 μg/ml, respectively, due to their limited solubilities.

Precision of this method was also investigated. Standards with known amount of formaldehyde and acetaldehyde were analyzed repeatedly up to 10 times. The relative standard deviation obtained for this method was 2.76%.

4. Conclusions

A method has been described for the determination of aldehydes in a basic medium, namely triethanolamine. While most aldehyde derivatization procedures are carried out under acidic conditions, this method provides the analyst with the additional capability of basic derivatization. This eliminates the need for any acidification of the sample prior to derivatization. The derivative products were found to be thermally stable and thus could be easily analyzed by GC. Excellent linearity of response with a correlation coefficient of 0.9998 was obtained, along with spike recoveries of greater than 90%, for all aldehydes studied.

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