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Note

Rapid separation and quantification of aliphatic carbonyl compounds by high-performance liquid chromatography using solvent programming

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The presence of carbonyl compounds in materials such as alcohols, glycols, or monomers is highly undesirable. In low-molecular-weight alcohols such as ethanol or propanol, the acrid odor of trace carbonyl compounds is evident even at the low ppm level. In high-molecular-weight alcohols employed as raw materials to manufacture plasticizers or detergents, traces or carbonyl compounds lead to undesirable properties such as color, odor, or reduced heat stability in the final product. Likewise, carbonyl contamination of monomers can result in monomer instability or reduced heat, light, and moisture resistance in the polymer end-product. A technique for rapid separation and quantification of a wide molecular weight range of aldehydes in such matrices is useful for studying the aforementioned problems caused by carbonyls.

Several reports have appeared on the separation of carbonyl compounds by gas chromatography. Among these is the work reported by Di Corcia *et al.*[1] using graphitized carbon black for analysis of low-boiling aldehydes. Hoshika and Muto[2] have published a technique for analysis of low-molecular-weight carbonyls by gas–liquid–solid chromatography. These techniques work with low-molecular-weight aldehydes but are not useful for the detection of high-molecular-weight species (C_6–C_{13} aldehydes and ketones) primarily because the low volatility of these compounds results in long analysis time and subsequently poor resolution. Selim[3] has published a high-performance liquid chromatography (HPLC) method for the determination of low-molecular-weight aldehydes by conversion to 2,4-dinitrophenylhydrazone derivatives and separation under isocratic conditions. Detection of aldehydes larger than C_5 was hampered by long retention under the isocratic elution with subsequent band broadening.

Described here is an HPLC procedure for the separation of aldehydes in the C_3–C_{13} range by gradient elution. The carbonyl compounds are quantitatively converted to the corresponding 2,4-dinitrophenylhydrazones and analyzed by solvent programmed C_{18} reversed-phase chromatography. The strong absorbance of the derivatives at 340 nm facilitates the use of UV detection. The high methylene group selectivity of reversed-phase chromatography results in excellent resolution of the various carbonyl derivatives. Gradient elution eliminated the problem of excessive retention of high-molecular-weight derivatives.

EXPERIMENTAL

Reagents and materials

2,4-Dinitrophenylhydrazine (2,4-DNP) was obtained from Eastman Organics (Stock No. 1866; Rochester, N.Y., U.S.A.) and recrystallized from ethanol. Aldehydes in the C_3 through C_{12} range were obtained from Pfaltz and Bauer (Stamford, Conn., U.S.A.).

Preparation of 2,4-dinitrophenylhydrazones

2,4-Dinitrophenylhydrazones were prepared as follows.

Two grams of 2,4-DNP were weighed into a 125-ml Erlenmeyer flask. A 10-ml volume of concentrated sulfuric acid was added, followed by the addition of distilled water until dissolution was complete. Two grams of the aldehyde were dissolved in 100 ml of purified ethanol and this solution was added to the 2,4-DNP solution. The crystalline derivatives formed were collected on a Buchner funnel and purified by recrystallization from ethanol two times.

Derivatization of trace aldehyde in a C_8 alcohol

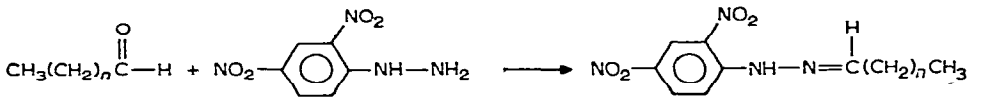
Approximately 2 g of a C_8 alcohol containing trace quantities of aldehyde were weighed into a 10-ml volumetric flask. Two ml of a 2,4-DNP solution (0.1 grams 2,4-DNP diluted to 100 ml with purified ethanol) were added along with two drops of 6 N HCl. The resulting solution was placed in a 50° water bath for 1 h. This assured quantitative conversion of aldehydes to their corresponding 2,4-dinitrophenylhydrazones. The solution was then cooled to room temperature and brought to volume with acetonitrile. This solution could then be injected directly into the liquid chromatograph after filtering.

Chromatographic conditions

A Perkin-Elmer Series 2/2 liquid chromatograph equipped with a Rheodyne 7120 injection valve and a Waters Model 440 absorbance detector set at 340 nm was used in this work. The column used was a pre-packed 30 cm × 3.9 mm I. D. μBondapak C_{18} column (Waters Assoc. Milford, Mass., U.S.A.). The mobile phase was acetonitrile–water.

RESULTS AND DISCUSSION

The conversion of the aldehydes to their corresponding 2,4-dinitrophenylhydrazones occurs via the following reaction:



The resulting hydrazones have an absorbance maximum at 340 nm. The molar extinction coefficient is independent of n. This absorbance is due only to the conjugated hydrazone linkage. The derivatization step is useful in discriminating against interferences since the reaction with 2,4-DNP is specific for carbonyls. Detection at 340 nm further aids in discrimination against matrix interferences since most

materials tested for carbonyl (alcohols, monomers) have little absorbance in this region.

The use of solvent programmed reversed-phase chromatography in conjunction with UV detection offers significant advantages over the spectrophotometric methods commonly employed for carbonyl analysis. Excess DNP reagent in the sample is separated from the hydrazone derivative, thus removing the blank absorbance reading required in spectrophotometric methods. Frequently the matrix, which may have some slight absorbance in the 340 nm region, is completely separated from the derivative. For example, a high-molecular-weight alcohol is eluted much more rapidly than the corresponding high-molecular-weight aldehyde derivative by virtue of its substantially lower molecular weight and higher polarity. Another advantage in the use of HPLC is that qualitative information about the aldehydes present in a sample can be obtained via the retention time.

In the analysis of octanol as described in the Experimental section for trace quantities of octanal, amounts as low as 1 ppm (1 μg octanal/g octanol) were detected using a 5-μl injection from the 10-ml final volume of the derivatization mixture. Detection limits could be pressed further by weighing more sample into the volumetric flask, increasing injection size, or working at a higher detector sensitivity. For our purposes, levels of aldehydes below 1 ppm were of little interest. Consequently, the ultimate detection limit of the technique was not estimated.

The qualitative capabilities of this technique are illustrated in Fig. 1 in which the separation of a mixture of C_3 through C_{12} aldehyde derivatives is achieved in under 10 min through the use of solvent programming. Initial solvent conditions were

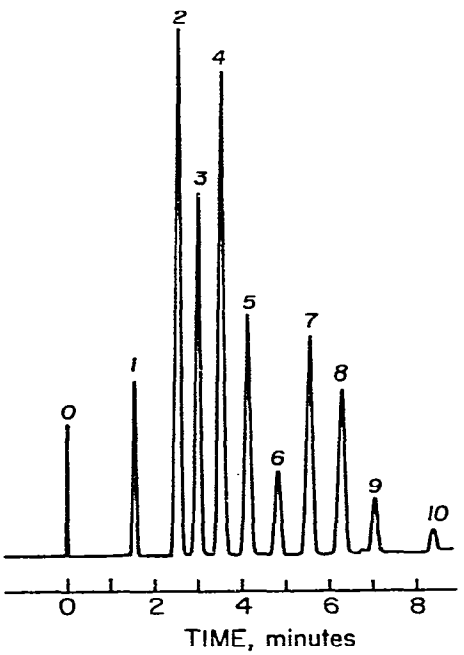


Fig. 1. Separation of DNP derivatives using solvent programming. Peak 0, chart marker; peak 1, 2,4-DNP reagent; peak 2, propionaldehyde derivative; peak 3, butyraldehyde derivative; peak 4, pentanal derivative; peak 5, hexanal derivative; peak 6, heptanal derivative; peak 7, ocatanal derivative; peak 8, nonanal derivative; peak 9, decanal derivative; peak 10, dodecanal derivative.

acetonitrile–water (70:30) at a flow-rate of 3 ml min^{-1}. The acetonitrile content was raised at a rate of 5% per min to 99%. This program solves the general elution problem for the aldehyde derivatives in the C_3–C_{12} range. A tabulation of the retention times for the aldehyde derivatives under the stated conditions is shown in Table I.

TABLE I

RETENTION TIMES OF VARIOUS ALDEHYDE DERIVATIVES

Compound	*Retention time (min)*
2,4 Dinitrophenylhydrazine	1.5
2,4-DNP derivative of:	
Propanal	2.5
Butanal	3.0
Pentanal	3.5
Hexanal	4.1
Heptanal	4.8
Octanal	5.5
Nonanal	6.3
Decanal	7.1
Dodecanal	8.3

The determination of carbonyl compounds by reversed-phase HPLC separation and UV detection of the 2,4-dinitrophenylhydrazones using gradient elution can be conveniently performed in a wide variety of matrices. HPLC offers distinct advantages over spectrophotometric methods in its ability to discriminate against interferences and in providing qualitative information about the sample.

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