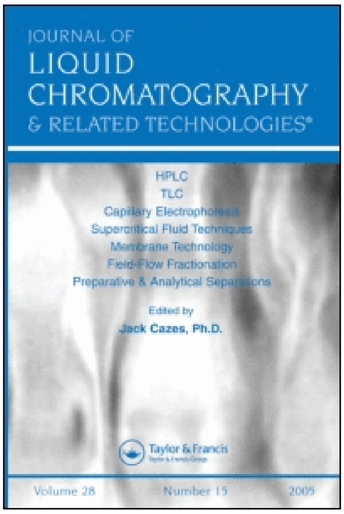

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Vapor-Phase Carbonyls by High-Pressure Liquid Chromatography

M. P. Maskarinec[a]; D. L. Manning[a]; P. Oldham[a]
[a] Analytical Chemistry Division Oak Ridge National Laboratory, Oak Ridge, Tennessee

To cite this Article Maskarinec, M. P. , Manning, D. L. and Oldham, P.(1981) 'Determination of Vapor-Phase Carbonyls by High-Pressure Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 4: 1, 31 — 39
To link to this Article: DOI: 10.1080/01483918108064794
URL: http://dx.doi.org/10.1080/01483918108064794

JOURNAL OF LIQUID CHROMATOGRAPHY, 4(1), 31-39 (1981)

DETERMINATION OF VAPOR-PHASE CARBONYLS BY HIGH-PRESSURE LIQUID CHROMATOGRAPHY

M. P. Maskarinec, D. L. Manning, and P. Oldham(1)
Analytical Chemistry Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

ABSTRACT

Methods have been developed for the trapping and quantitative analysis of low molecular weight carbonyls in complex gas phase mixtures. Formaldehyde, acetaldehyde, acrolein, and acetone are separated as the 2-4-dinitrophenylhydrazones with a sensitivity of less than 10 ppb. The separation can be done on a variety of commercial C_{18} reverse-phase columns.

INTRODUCTION

Carbonyl compounds from one to four carbon atoms present a significant environmental hazard. Formaldehyde has recently been declared a carcinogen (by the National Cancer Institute); acetaldehyde and acrolein are well-established ciliatoxic and cytotoxic agents (2), and acetone has demonstrated toxicity although at somewhat higher levels. In addition, the Occupational Safety and Health Administration (OSHA) has established limits for exposure to formaldehyde (.5 ppm) and acrolein (.1 ppm) as well as acetone (500 ppm) (3). These levels require the development of specific and sensitive analytical methods.

Classically, carbonyl compounds have been determined using colorimetry. Derivatives such as oximes, semicarbazones, and phenylhydrazones are easily formed, and can be used as qualitative indicators of carbonyl content. However, the determination of specific carbonyls requires some separation system. With the exception of formaldehyde, the carbonyls of interest in this work are easily vaporized and thus amenable to gas chromatography. Several approaches have been in use for some time, including direct introduction of gas samples with or without cryogenic focusing(4,5) and "purge and trap" injection of aqueous samples.

Gas chromatographic determination of these compounds is of limited utility, for several reasons. The inherent lack of sensitivity precludes the analysis of acrolein at subpart-per-million levels. Precision and accuracy are impaired due to volatility and reactivity considerations, and direct standardization is difficult. Thus, improvement of the methodology is imperative if the determination of these compounds is to be performed on a routine basis, as may be required under OSHA guidelines.

An alternative approach has been to take advantage of the reactivity of these compounds for the formation of absorbing derivatives, followed by separation using HPLC. The 2,4-dinitrophenylhydrazones are easily formed, stable, and highly absorbing. In addition, these derivatives are of low volatility, making sample concentration feasible. Finally, the carbonyls of interest have been separated on reverse-phase columns as the 2,4-dinitrophenylhydrazones (6).

The primary objective of this work has been to provide quantitative definition of the methodology, particularly with respect to trapping efficiency and recovery. This has been done by comparison with established gas chromatographic methods. A second objective has been to establish adequate separation systems with a variety of reverse phase columns, in order to provide a working guide for those interested in the determination. The third objective has been to demonstrate the utility of this approach using complex environmental samples.

MATERIALS AND METHODS

Reference samples of the carbonyls were obtained from commercial sources at the highest available purity. The 2,4-dinitrophenylhydrazine was obtained from J. T. Baker Chemical Company. All solvents were reagent grade or better, and were distilled in glass prior to use. Reverse phase columns were obtained prepacked from the various vendors.

Standard 2,4-dinitrophenylhydrazones were prepared in bulk form and recrystallized twice from hot methanol. The purity was checked by HPLC. The standards were dissolved in methanol on a weight/volume basis and stored frozen. Solutions prepared in this manner were stable for several months.

Trapping of the gas-phase carbonyls was accomplished by adding 20 ml of saturated 2,4-dinitrophenylhydrazine in 2 N HCl and 20 ml chloroform to a 1 L gas sampling flask. The flasks were then evacuated, and the carbonyls added. Cigarettes were smoked under standard analytical conditions (1 puff/minute, 35 ml puff volume, to a butt length of 23 mm) using a Filamatic single port smoker (7). Diesel fuel aerosols were introduced directly into the sampler.

High-pressure liquid chromatography was done using a variety of equipment. Injection was done either by use of a Rheodyne Model 7020 loop injector or a Waters WISP-710 Autosampler. Waters Model 6000A pumps were used, and detection was by UV with either a Waters Model 440 fixed wavelength detector or a Varian variable wavelength detector. All columns were C_{18} reverse-phase, obtained from various commercial sources.

RESULTS AND DISCUSSION

The separtion of the DNPHs of formaldehyde, acetaldehyde, acrolein and acetone was compared on a series of reverse phase columns (Table 1). All columns tested gave adequate separation for the compound of interest. With slight variations in the mobile phase composition, analysis times were roughly equivalent. We believe that any reasonably efficient C_{18} column will perform this separation. The degree of separation can be imrpoved by using weaker mobile phases at the expense of increased analysis time (Figure 1).

Detection can be performed at either 254 nm or 350 nm. For highest sensitivity with reasonably clean gas samples (filtered), 254 nm is best. However, for complex aerosols, better selectivity is obtained at 350 nm at about a 20% decrease in sensitivity. Fluorescence detection further improves the selectivity, but does not offer any significant increase in sensitivity. Thus, all experiments were carried out at 254 nm. The ultimate sensitivity (roughly equivalent for all carbonyls) is 10 ng injected on column.

The use of HPLC for the quantitative analysis of these compounds demands adequate conversion of the carbonyls to the derivatives during trapping. However, the extreme volatility and reactivity of the compounds makes assessment of the conversion efficiency quite difficult. For this reason, comparisons were made using cigarette smoke. The direct determination of these compounds by GC, even though suffering the limitations mentioned earlier, has been carried out in this laboratory for

TABLE 1

Conditions for the Separation of Carbonyls on Various Commercial C_{18} Columns

Column	Dimensions	Flow Rate	Mobile Phase (methanol/water)
Partisil-10-ODS-2 (Whatman)	2.5 cm x 4.6 mm	1.0 ml/min	60/40
Zorbax-ODS (Dupont)	2.5 cm x 4.6 mm	1.0 ml/min	70/30
HC-Sil-ODS (Perkin-Elmer)	2.5 cm x 4.6 mm	1.0 ml/min	65/35
Bio-Sil-HP-10 Reverse Phase (Bio-Rad)	2.5 cm x 4.6 mm	1.0 ml/min	60/40

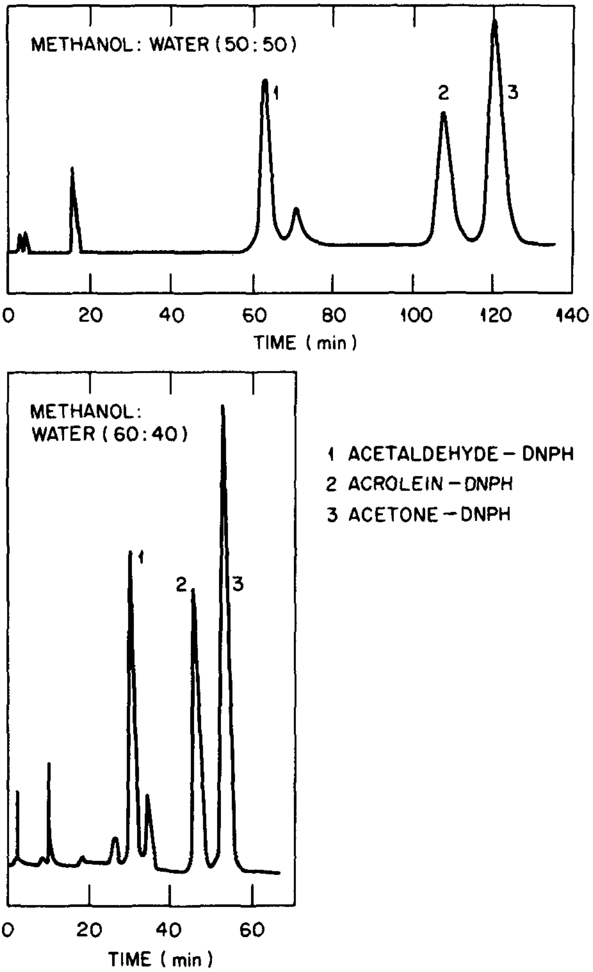

FIGURE 1. Effect of Mobile Phase on the Separation of Carbonyls. Column: Partisil 10 ODS-2. Flow Rate: 1 ml/min.

many years. The values for acetaldehyde and acrolein are thus well established, and recovery calculations based on known deliveries of reference cigarettes are possible (4).

For determination of trace levels of the carbonyls in ambient atmospheres, a flow-thru trapping system would be preferable. This type of system would allow the sampling of large volumes of air, with concentration of the carbonyls. We thus tested several trapping systems with varying sampling rates, reagent volumes, and sampling stages. However, under our conditions, we were not able to recover more than 20 to 40% of the acrolein from the gas stream. Under high flow conditions significant breakthrough occurred, even when additional traps were used. Under low flow conditions, the aldehydes apparently react to form higher molecular weight adducts (Figure 2) which are detected as later eluting peaks in the chromatogram. The best recoveries were obtained using liquid nitrogen cold traps with subsequent addition of the reagents, and even with these conditions the recovery was poor for acrolein.

Therefore, a closed trapping system was adopted which permitted the introduction of one liter of gas into an evacuated bulb containing the reagent (saturated 2,4-dinitrophenylhydrazine in 2 N HCl) and extract-

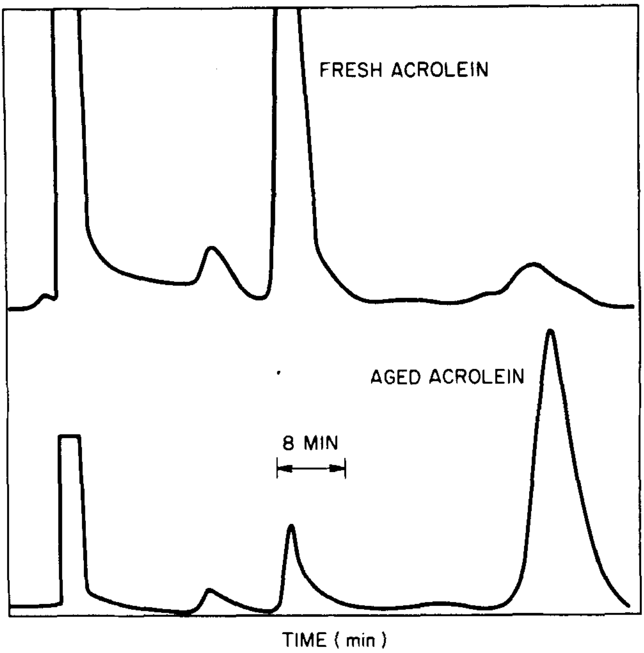

FIGURE 2. Effect of Ageing at Room Temperature on the Chromatogram of Acrolein-DNPH. Fresh Acrolein: Reagent stored at 10°F, derivatized. Aged Acrolein: Same reagent after standing at room temperature three days, derivatized.

ant ($CHCl_3$). After sampling, the bulb was shaken for 30 minutes, the organic layer was separated, and adjusted to a known volume. Recovery of the carbonyls using this system was of the order of 80% for acrolein, 90% for acetaldehyde, and 95% for acetone. The reproducibility was excellent. Further studies were performed in order to maximize recovery, and the best conditions were those listed.

The application of this methodology to the determination of carbonyls in cigarette smoke is shown in Figure 3. The results obtained

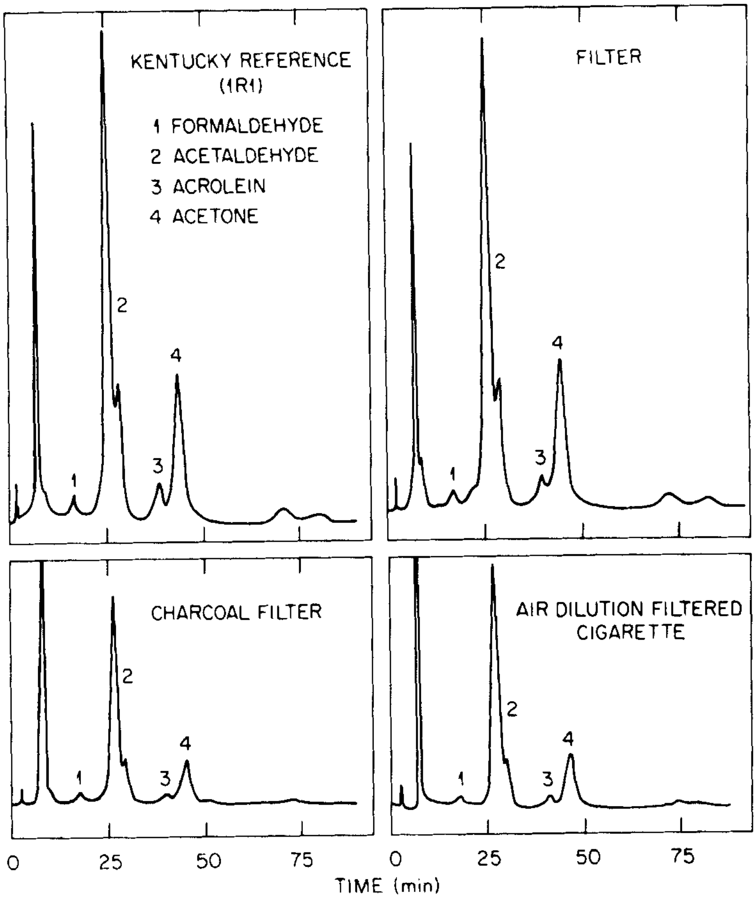

FIGURE 3. Carbonyl Profiles for Selected Cigarettes. Column: Partisil 10 ODS-2. Mobile Phase: Methanol:Water (60:40). Flow Rate: 1 ml/min.

were in good agreement with established values, indicating the quantitative reliability of the technique. Levels were highest in non-filter cigarettes and lowest in cigarettes using charcoal filters. Significant improvements over direct GC determination were made in sample throughput and sensitivity. Recent work has indicated that even the lowest commercial cigarettes (>.1 mg tar) contain detectable amounts of the carbonyls when measured in this way.

The extension of this methodology to other combustion mixtures is shown in Figure 4. Diesel fuel was aerosolized in a hot manifold and the resulting gases trapped. When no air was present (Figure 4a), the levels of the carbonyls were much lower than those found when air was present (4b), indicating the nature of formation of these compounds. While the presence of air increases the formation of all vapor phase carbonyls, acrolein and formaldehyde are markedly increased. Sampling of ambient air in a similar fashion resulted in a wide range of

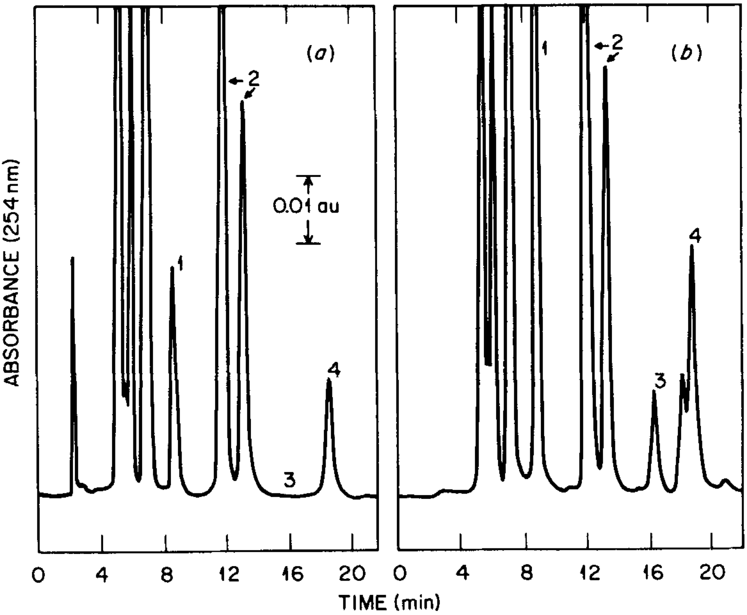

FIGURE 4. Carbonyl Profile of Diesel Fuel Aerosol. Curve numbers per Figure 3. Oxygen: (a) Absent, (b) Present. Column: Dupont Zorbax ODS. Mobile Phase: Methanol:Water (70:30). Flow Rate: 1 ml/min.

acrolein values, from 40 ppb to >50 ppm. Detection limits for acrolein using the current system are lower than the established OSHA exposure limits, permitting accurate assessment of occupational exposure.

In conclusion, quantitative trapping techniques combined with analysis by HPLC have been developed which provide enhanced sensitivity and increased sample throughput in the determination of the C_1-C_5 carbonyls. (Although not the purpose of this work, the techniques can also be extended to the analysis of higher molecular weight carbonyl compounds.) The determination provides sensitivity in excess of current OSHA standards, and should be of value to those concerned with compliance to workplace standards.

ACKNOWLEDGMENT

We acknowledge the collaboration of R. W. Holmberg and J. H. Moneyhun for generation of the diesel fuel aerosols.

Research sponsored by the National Cancer Institute under Interagency Agreement DOE (ERDA/AEC) 40-485-74, NIH (NCI) Y01-CP-60206, with the U. S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

REFERENCES

1. Student, Freed-Hardeman College, Henderson, Tennessee.

2. Wynder, Ernest L., and Hoffmann, Dietrich, Tobacco and Tobacco Smoke, Academic Press, New York, 1967, pp. 407-418.

3. Federal Register, Environmental Protection Agency, Part III. Guidelines Establishing Test Procedures for Analysis of Pollutants, Proposed Regulations, 44, 79, 1979.

4. Horton, A. D., and Guerin, M. R., Determination of Acetaldehyde and Acrolein in the Gas Phase of Tobacco Smoke Using Cryothermal Gas Phase Crhomatography, Tob. Sci., 176, 19, 1974.

5. Zeldes, S. G., and Horton, A. D., Trapping and Determination of Labile Compounds in the Gas Phase of Tobacco Smoke, Anal. Chem., 50, 779, 1978.

6. Kuwata, Hazukiro, Uebori, Michiko, and Yamasaki, Yoshiaki, Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs As Their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography, J. Chromatorg. Sci., 17, 264, 1979.

7. Guerin, M. R., and Shults, W. D., Tobacco Smoke Analysis Program Progress Report for the Period January 1, 1970, to September 1, 1970. ORNL-4642, January 1971, p. 5.