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DIRECT DETERMINATION OF OXYGENATED COMPOUNDS IN COMPLEX MIXTURES BY CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A method has been developed for the direct determination of oxygenated compounds in complex mixtures by capillary gas chromatography on a fused-silica column, coated with a polar stationary phase. Compounds identified and determined without derivatization include carboxylic acids, primary alcohols, *n*-aldehydes, methyl esters and ketones. The chromatographic system consists of a fused-silica capillary column, 50 meters in length, with a coating of AT-1000 (FFAP). The selectivity of this phase enables the separation of the oxygenated compounds from the hydrocarbons in these complex mixtures and distributes them by molecular weight into characteristic peak envelopes for each class of oxygenate. The free carboxylic acids peaks elute with minimal tailing and adsorption.

INTRODUCTION

Since the 1973 oil crisis, there has been increased interest in the production of synthetic fuels, namely engine fuels and oxygenated products. In the reactions that form these synthetic fuels, mixtures of hydrocarbons and oxygenated compounds are produced catalytically at various temperatures and pressures. Conditions and catalysts may be changed to produce complex mixtures that are either essentially hydrocarbons, or are hydrocarbon mixtures enriched in oxygenated compounds. These oxygenated compounds include carboxylic acids, alcohols, aldehydes, ketones and esters.

Despite the wide use of derivatization procedures in the analysis of carboxylic acids, there still exists a need for separating these acids in their free form.

Carboxylic acids have been analyzed in most laboratories on packed columns, although the first paper on the capillary gas chromatographic (GC) analysis of acids was published by Lipsky *et al.*[1] as early as 1959. Because of the considerable polarity of the carboxylic acid group (R–COOH) and its capability of forming hydrogen bonds, the separation of acids in the free form is difficult, due to strong interactions which in turn lead to adsorption or peak tailing[2]. This has usually been avoided by converting the acids to their corresponding methyl esters. However, the esterification step lengthens the overall analytical procedure and may in some cases alter the analytical results[3]. For these reasons, a direct analysis is desirable.

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This paper describes a capillary GC method that has been developed for the identification and direct determination of the oxygenated compounds, including carboxylic acids, in complex mixtures, by the use of a fused-silica capillary column. The entire chromatographic system is essentially fused silica since the injection port of the gas chromatograph is fitted with a special fused-silica split liner. This liner shows greater deactivation and less sample adsorption compared to conventional glass liners. The minimal peak tailing and excellent peak shapes for the oxygenates, and the carboxylic acids in particular, confirm that the deactivation is effective.

EXPERIMENTAL

The gas chromatograph initially used for this method development was a Varian Model 3700 equipped with dual flame ionization detectors. The method was later transferred to a Hewlett-Packard Model 5880 equipped with an automatic liquid sampler, dual flame ionization detectors, and electronic pneumatic control of the capillary inlet system with pressure programming capability. Both gas chromatographs were also interfaced to a Hewlett-Packard Model 3357 laboratory automation system for data accumulation and reduction. The fused-silica capillary (wall-coated open tubular) column used was 50 m in length, 0.25 mm internal diameter, and coated with a 0.2-μm film of AT-1000 (Alltech Associates). AT-1000 is a free fatty acid phase (FFAP), which is a reaction product of 2-nitroterephthalic acid and Carbowax 20M. Other liquid phases such as Carbowax 20M and OV-1701, were screened before choosing the AT-1000 phase. The AT-1000 was chosen because it gave the best acid peak shapes. The GC parameters used with the Varian Model 3700 were as follows: Oven temperature, 45°C (4 min), 45°C to 210°C at 5°C/min, 210°C (8 min); injection port temperature, 240°C; flame ionization detector temperature, 240°C; sample size, 0.5 μl; carrier gas, helium; injection mode, split; splitting ratio, 130:1; carrier gas linear velocity, 20 cm/sec; column flow, 0.6 ml/min. The GC parameters used with the Hewlett-Packard Model 5880 were as follows: Oven temperature, 40°C

TABLE I

RETENTION TIME REPRODUCIBILITY IN THE SPLIT MODE WITH ELECTRONIC PRESSURE PROGRAMMING AND AN AUTOMATIC LIQUID SAMPLER
Sample: 0.2 μl, calibration blend of C_2–C_{10} carboxylic acids.

Peak	*Retention times for replicate runs (min)*						*Mean retention time (min)*	*Relative standard deviation (%)*
	1	*2*	*3*	*4*	*5*	*6*		
C_2 acid	19.03	19.04	19.03	19.03	19.04	19.03	19.03	±0.005
C_3 acid	21.46	21.48	21.47	21.47	21.47	21.48	21.47	±0.007
C_4 acid	23.85	23.86	23.86	23.85	23.86	23.86	23.86	±0.005
C_5 acid	26.63	26.63	26.64	26.62	26.62	26.64	26.63	±0.009
C_6 acid	29.20	29.19	29.20	29.21	29.20	29.20	29.20	±0.006
C_7 acid	30.35	30.35	30.35	30.36	30.36	30.35	30.35	±0.005
C_8 acid	33.88	33.87	33.87	33.88	33.88	33.88	33.88	±0.005
C_9 acid	36.00	35.98	36.00	35.99	35.98	36.00	35.99	±0.010
C_{10} acid	38.05	38.04	38.04	38.05	38.03	38.05	38.04	±0.008

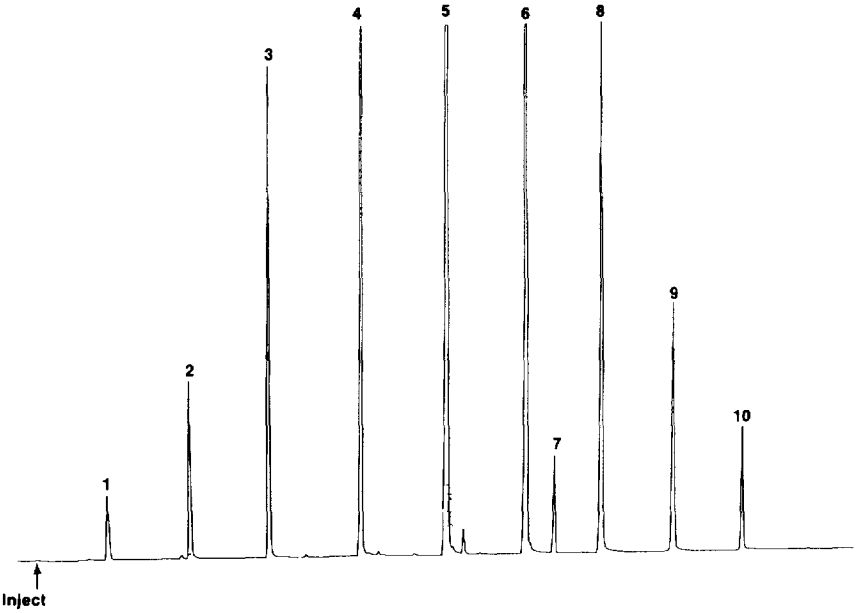

Fig. 1. Aqueous calibration mixture of aliphatic *n*-carboxylic acids. Peaks: 1 = acetic acid; 2 = propionic acid; 3 = butyric acid; 4 = pentanoic acid; 5 = hexanoic acid; 6 = heptanoic acid; 7 = biphenyl (internal standard); 8 = octanoic acid; 9 = nonanoic acid; 10 = decanoic acid.

(5 min), 40°C to 80°C at 5°C/min, 80°C (1 min), 80°C to 210°C at 5°C/min, 210°C (15 min); pressure program, 200 kPa (5 min), 200 kPa to 350 kPa at 5 kPa/min, 350 kPa (25 min); injection port temperature, 240°C; flame ionization detector temperature, 240°C; sample size, 0.2 μl; carrier gas, helium; injection mode, split; splitting ratio, 250:1; carrier gas linear velocity, 37 cm/sec; column flow, 1.0 ml/min.

The injection ports of both of the gas chromatographs were fitted with fused-silica liners for split sample introduction. For the Varian Model 3700, the liner was the baffled type, and was obtained from Varian. The Hewlett-Packard Model 5880 liner used was a splitless liner packed with phosphoric acid-treated glass wool. These silica liners proved to be the best for samples that were adsorptive and of wide boiling range. The combination of the fused-silica liner and a fused-silica capillary column provided a completely inert and deactivated system and minimized adsorptive interactions with samples.

RESULTS AND DISCUSSION

Fig. 1 shows a calibration chromatogram of aliphatic *n*-carboxylic acids ranging from C_2 to C_{10}, with biphenyl as the internal standard. The acid peaks eluted with minimal tailing and adsorption. This is due to the chromatographic system being essentially all fused-silica. Since the column was 50 meters in length, the greater residence time of mixtures on the column surface required an inert, deactivated fused-silica system.

The Hewlett-Packard 5880 gas chromatograph was equipped with an auto-

TABLE II

OXYGENATE DETERMINATION CALIBRATION TABLE

Retention time (min)	*Component name*	*Retention time (min)*	*Component name*
2.56	Acetaldehyde	13.92	Methyl heptanoate (C_7)
2.79	Methyl formate (C_1)	16.57	1-Hexanol
2.89	Propionaldehyde	16.81	Methyl caprylate (C_8)
3.07	Acetone	18.56	1-Heptanol
3.11	Ethyl formate	19.03	Acetic acid (C_2)
3.15	Methyl acetate (C_2)	19.47	Methyl pelargonate (C_9)
3.22	Diisobutyl ether	20.64	Isobutyric acid
3.53	*n*-Butyraldehyde	21.46	Propionic acid (C_3)
3.71	Methanol	21.85	1-Octanol
3.78	Methyl propionate (C_3)	21.99	Methyl decanoate (C_{10})
3.80	Methyl ethyl ketone	23.20	Isovaleric acid
3.92	3-Methyl-2-butanone	23.85	Butyric acid (C_4)
4.25	Ethanol	24.21	1-Nonanol
4.56	Ethyl propionate	24.35	Methyl undecanoate (C_{11})
4.98	Methyl butyrate (C_4)	26.63	Pentanoic acid (C_5)
5.19	*n*-Valeraldehyde	26.74	1-Decanol
5.44	Diisopropyl ketone	26.89	Methyl laurate (C_{11})
5.64	4-Methyl-2-pentanone	29.20	Hexanoic acid (C_6)
5.84	Isobutyl acetate	29.70	Methyl tridecanoate (C_{13})
6.36	Ethyl butyrate	30.35	Heptanoic acid (C_7)
6.70	1-Propanol	30.74	Methyl myristate (C_{14})
7.60	Methyl valerate (C_5)	30.80	Biphenyl (internal standard)
7.79	2-Methyl-1-propanol	33.88	Octanoic acid (C_8)
8.02	Isobutyl isobutyrate	34.01	Methyl pentadecanoate (C_{15})
8.16	*n*-Hexanal	36.00	Nonanoic acid (C_9)
8.28	Methyl crotonate	38.05	Decanoic acid (C_{10})
8.69	2-Pentanol	38.33	Methyl heptadecanoate (C_{17})
10.15	1-Butanol	38.91	Methyl stearate (C_{18})
10.81	Methyl caproate (C_6)	39.86	Methyl nonadecanoate (C_{19})
11.19	3-Hexanol	42.04	Methyl eicosanoate (C_{20})
13.56	1-Pentanol		

matic liquid sampler and an electronic pneumatic control of the carrier gas for the capillary inlet system. These features permitted total automation of the determinations. The reproducibility of retention times in the split mode was extremely good (see Table I), with standard deviations typically less than $\pm 0.010\%$.

By using electronic pressure programming of the carrier gas, a constant linear velocity was maintained through the column as the temperature was increased and shorter analysis times were obtained.

The oxygenated compounds identified in complex mixtures include C_2–C_{10} aliphatic *n*-carboxylic acids, C_1–C_{20} primary alcohols, C_2–C_6 *n*-aldehydes, ketones in the C_4 range and C_1–C_{20} methyl esters. Retention times and names of calibrated peaks analysed using this method are listed in Table II. The data has been included in a computerized analysis by the HP-3357 automation system which calculates weight percentages for all the calibrated components based on an internal standard, biphenyl. Low levels of detection have been achieved for the oxygenated compounds,

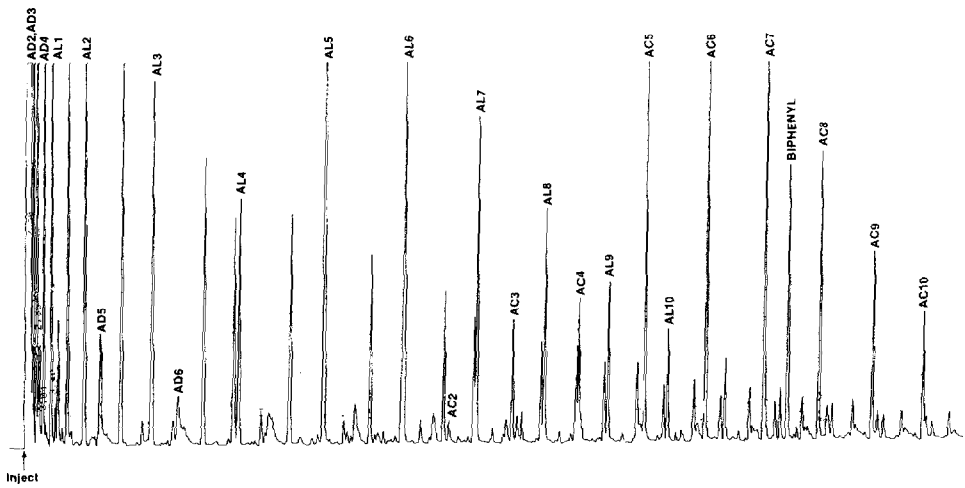

Fig. 2. Complex oxygenate mixture. Peak identification: Ad = aldehyde, with carbon number, AL = alcohol, with carbon number; AC = carboxylic acid, with carbon number.

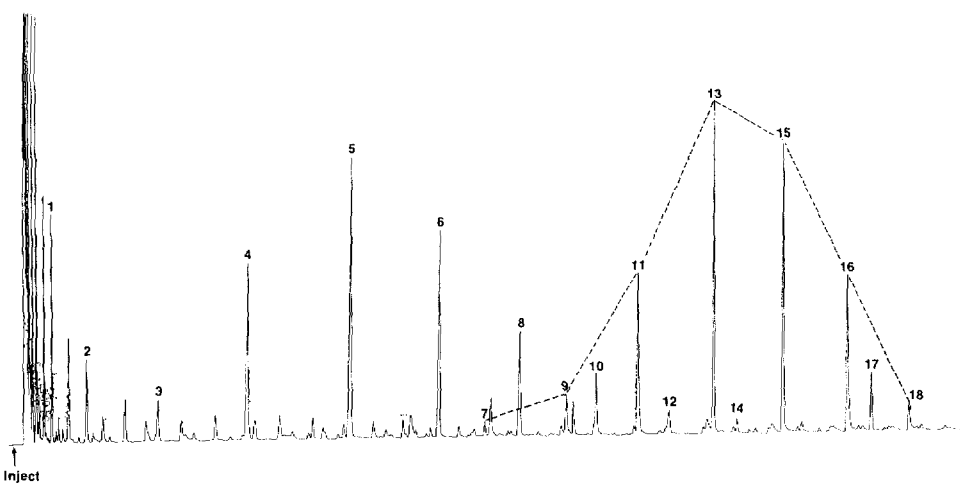

Fig. 3. Complex oxygenate mixture. Peaks: 1 = methanol; 2 = ethanol; 3 = 1-propanol; 4 = 1-butanol; 5 = 1-pentanol; 6 = 1-hexanol; 7 = acetic acid; 8 = 1-heptanol; 9 = propionic acid; 10 = 1-octanol; 11 = butyric acid; 12 = 1-nonanol; 13 = pentanoic acid; 14 = 1-decanol; 15 = hexanoic acid; 16 = heptanoic acid; 17 = biphenyl (internal standard); 18 = octanoic acid.

particularly for the acids, which have been determined to have concentrations as low as 5 ppm.

Figs. 2 and 3 show chromatograms for the oxygenate determination of actual mixtures. The selectivity of the polar AT-1000 phase of the fused-silica capillary column allowed the separation of the oxygenated compounds from the hydrocarbons in these complex mixtures. The hydrocarbons typically encountered were normal straight chain alkanes and 1-alkenes ranging from C_4 to C_8. Since the hydrocarbons

are less polar than the oxygenated compounds, they were essentially unretained by the stationary phase and eluted early. In addition, the oxygenate peaks were distributed by molecular weight into characteristic envelopes for each class of oxygenates. Because of this ability to distribute oxygenated compounds into characteristic envelopes, with an analysis time less than 60 min, this method can be used as a rapid screening tool for a variety of essentially unknown complex mixtures.

Fig. 3 shows the envelope drawn over the class of carboxylic acids. Similar envelopes can be observed for the alcohols, aldehydes and esters.

CONCLUSIONS

A capillary GC method has been described for the direct determination and identification of oxygenates in complex hydrocarbon mixtures with no derivatization necessary. Peaks were eluted with minimal tailing and adsorption. Necessary deactivation was achieved by the use of fused-silica liners and capillary columns. Small samples sizes were required (0.2–0.5 μl) with analysis times under one hour. With the proper choice of capillary column and instrumental conditions, classes of oxygenated compounds were distributed by molecular weight into characteristic envelopes. Excellent reproducibility of retention times was achieved when an automatic sampler and electronic pressure programming of the carrier gas were used.

Work is underway on the determination of oxygenated compounds in complex mixtures with a dual-column system. This procedure involves the use of polar and non-polar capillary columns for the positive identification of oxygenated compounds as well as the determination of hydrocarbons.

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