Journal of Chromatography, 202 (1980) 255–261
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,231

GAS CHROMATOGRAPHY OF SIMPLE MONOCARBONYLS IN CIGARETTE WHOLE SMOKE AS THE BENZYLOXIME DERIVATIVES

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(Received July 2nd, 1980)

SUMMARY

A qualitative and semi-quantitative method was established for the investigation of low-molecular-weight volatile carbonyl compounds in cigarette whole smoke. The carbonyls were trapped on a silica gel "column" and eluted with water. The aqueous solution was then treated with benzyloxyamine to form the corresponding oximes, which were then separated on a short (12 m) FFAP glass-capillary gas chromatographic column with temperature programming, and detected by a nitrogen selective detector. An internal standard was added both as a reference for retention time determinations, and as an aid in estimating the amounts of the individual carbonyls in the smoke samples.

INTRODUCTION

The detection and analysis of volatile carbonyl compounds in complex matrices have been investigated rather extensively and reported in the literature. Usually, these carbonyls have been analyzed as their 2,4-dinitrophenylhydrazones (2,4-DNPHs), using paper, column, thin-layer, gas and liquid chromatography as separation techniques.

Shibasaki and Iwabuchi[1] have determined these compounds in "miso" aroma; Shimizu *et al.*[2] in roasted starch; Kallio and Linko[3] in arctic bramble, Pyysalo[4] and Hirrsalmi *et al.*[5] in hybrids between raspberry and arctic bramble; Linko *et al.*[6] in carrots; and Bachmann *et al.*[7] in urine. The analysis of simple carbonyl compounds in tobacco smoke has also been the subject of much attention, for about the last 25 years[8–18], again with the majority of determinations made using the 2,4-DNPHs. More recently, a method was described for the preparation of benzyloxime derivatives of simple monocarbonyls[19], and the work described here applies that method for the use of benzyloxime derivatives to the analysis of carbonyls in cigarette smoke.

Briefly, the cigarette whole smoke was passed through a silica gel column to trap the carbonyls, followed by elution with water. The carbonyls were then converted to the corresponding oximes, which were extracted into diethyl ether. Separation of the oximes was accomplished by temperature-programmed glass-capillary gas chromatography (GC) on a short (12 m) FFAP column. An internal standard was added

0021-9673/80/0000–0000/$02.25

both as a reference for retention time determinations, and as an aid in estimating the amounts of the individual carbonyls in the smoke samples.

EXPERIMENTAL

Smoke trapping

Smoke absorption traps were constructed as in Fig. 1. Part B was filled with 5.5 g of silica gel (Grade 408, 12–28 mesh, Davison Chemical, Baltimore, MD, U.S.A.), gently tamped to a 100-mm column and held in place by two pieces of glass wool. The silica gel was positioned about 5 mm from the open end of the tube, where the cigarette was fitted for smoking. The assembled trap (Fig. 2) was connected in a horizontal alignment to a syringe-type smoking machine in place of the Cambridge filter pad. In this manner, the whole smoke was drawn through the silica gel trap.

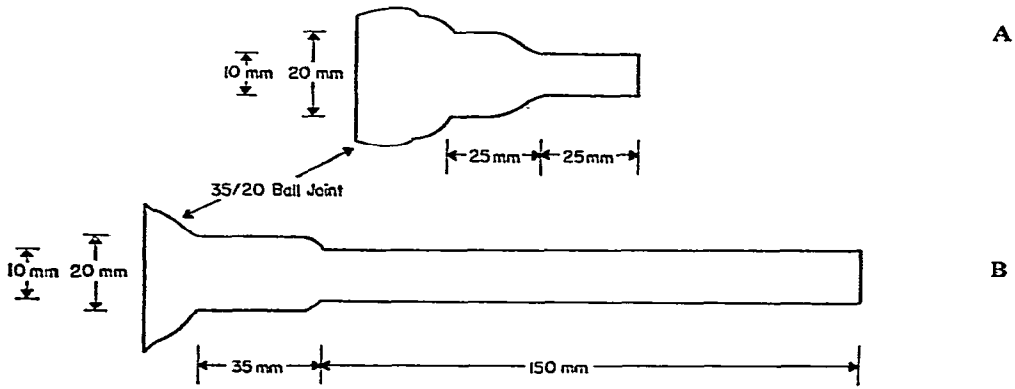

Fig. 1. Smoke absorption trap, dimensions.

Smoking conditions

Standard smoking conditions were used: The cigarettes were conditioned at 25°C and 60% relative humidity and smoked, taking a 35-ml puff of 2 sec duration each minute, to a 30-mm butt length. Three cigarettes were smoked into each trap.

Internal standard solution

An aqueous solution was prepared to contain about 80 μg of hexanal per milliliter of solution.

Sample preparation

Following smoking, part B of the trap was disconnected and clamped in a vertical position with the ball joint end up; in this manner it functioned as a column for the elution of the carbonyls (Fig. 3). A 1-ml volume of the hexanal internal standard solution was added to the top of the column and the carbonyls eluted with water. About 15 ml were collected in a screw-capped bottle, and the benzyloximes prepared as reported earlier[19], whereby the oximes are isolated in diethyl ether.

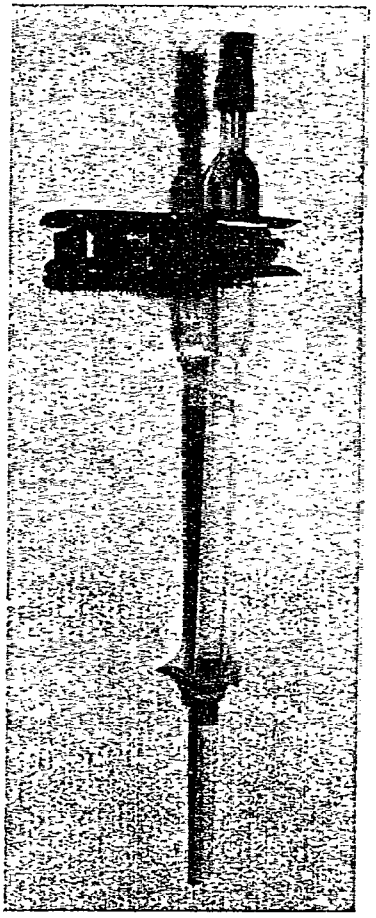

Fig. 2. Smoke absorption trap, assembled for smoke collection.

Gas chromatography

The GC conditions were identical to those previously reported[19] for the benzyloxime derivatives of short-chain carbonyls.

RESULTS

Fig. 4 shows a representative scan of the carbonyls of whole smoke from three Kentucky Reference 2R1 cigarettes (research cigarettes produced for the University of Kentucky Research Foundation). (A more extensive listing of retention times of carbonyl benzyloximes can be found in ref. 19.)

Table I illustrates experimental values determined for several carbonyls in the smoke of three commercially available cigarettes, as determined as the benzyloximes. The average as well as the range of values obtained are given; each average is the result of at least four, and in some cases as many as eight, determinations.

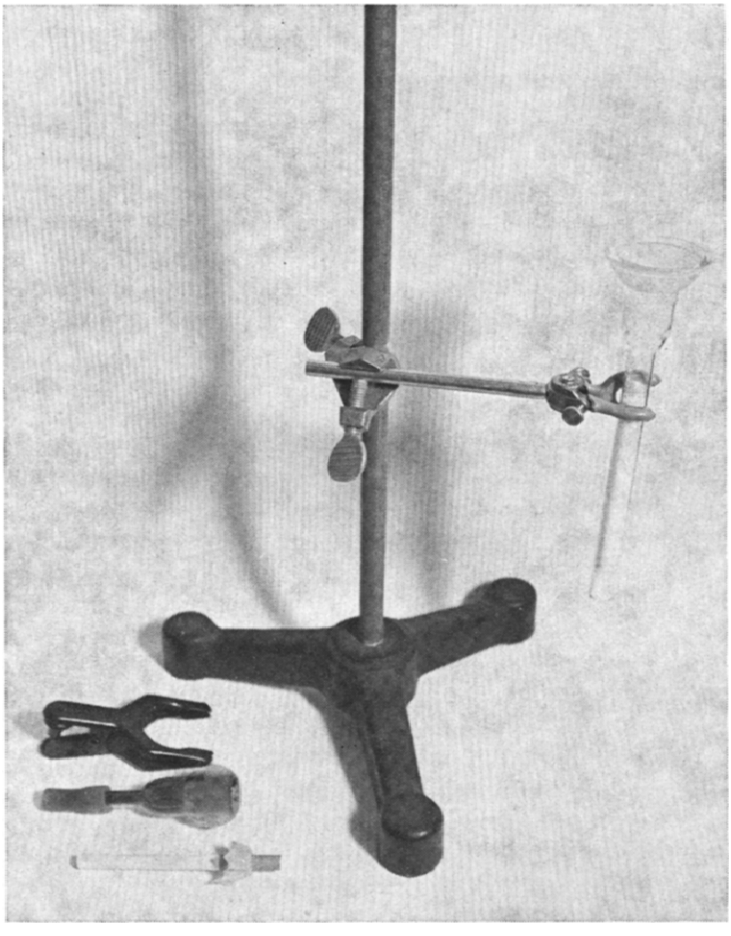

Fig. 3. Smoke absorption trap, assembled for elution.

TABLE I

LEVELS OF SELECTED CARBONYLS IN THE WHOLE SMOKE OF SOME CIGARETTES

Levels are tabulated as average; values in parentheses indicate the range. The values are given in μg/cigarette.

	Cigarette A (filter)	*Cigarette B (filter, low delivery)*	*Cigarette C (non-filter)*
Formaldehyde	31(10–50)	10(9–10)	21(12–30)
Acetone	400(325–475)	137(130–144)	330(310–350)
Propanal	61(37–100)	37(30–40)	50(50–53)
Acrolein	23(13–37)	3(3–4)	22(20–25)
Methacrolein	17(14–38)	18(18–19)	27(20–32)
Butanal	20(9–29)	13(12–13)	18(17–20)

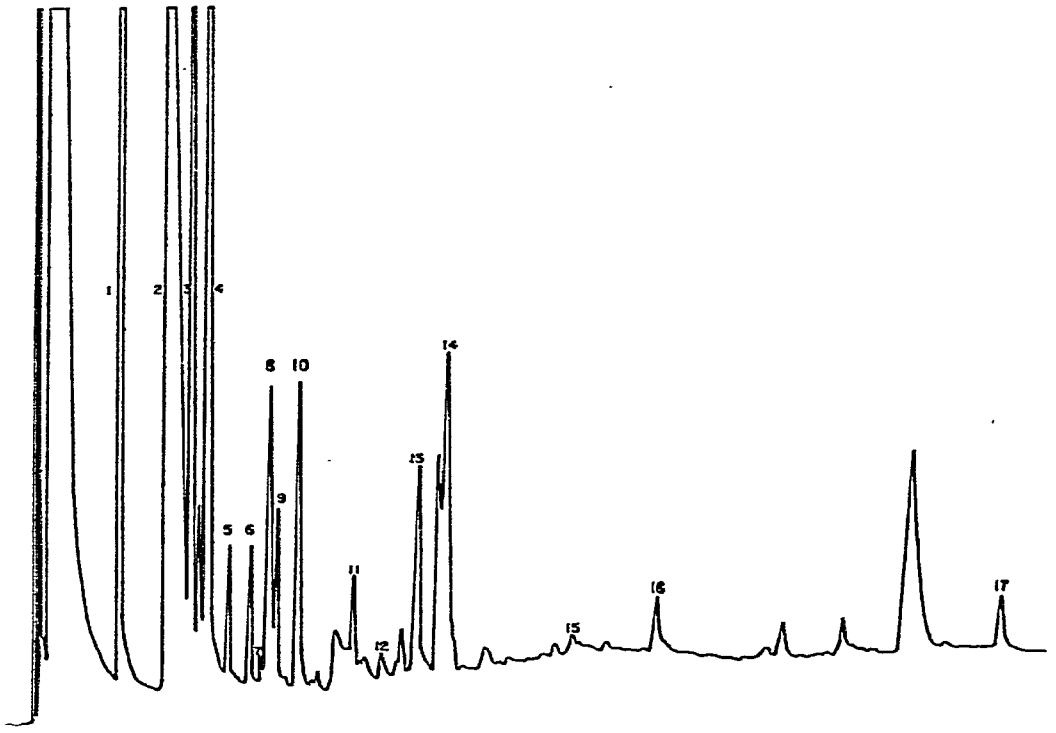

Fig. 4. GC scan of benzyloximes of some carbonyls in Kentucky Reference 2R1 cigarette whole smoke. For chromatographic conditions, see ref. 19. Peak identification is based on retention time relative to the hexanal compound. Peaks: 1 = formaldehyde; 2 = acetaldehyde; 3 = propanal; 4 = acetone; 5 = butanone; 6 = propenal (acrolein); 7 = pentanone (2- and/or 3-); 8 = butanal; 9 = methacrolein; 10 = isopentanal; 11 = pentanal; 12 = 5-hexen-2-one; 13 = 2-butenal (crotonaldehyde); 14 = hexanal; 15 = cyclohexanone; 16 = 2-hexenal and/or cycloheptanone; 17 = benzaldehyde.

DISCUSSION

Optimization of conditions

In the development of the method, several variables were evaluated to optimize conditions.

Collection of carbonyls from smoke. Several methods of collecting the carbonyls from cigarette smoke were investigated, including bubbling the smoke through liquid traps similar to those described by Mansfield *et al.*[18]. The silica gel traps described in Experimental were found to be the method of collection giving the highest efficiency while still retaining the puff characteristics best in terms of least-pressure drop during smoking.

Number of cigarettes per trap. It was found that the amount of the individual carbonyls recovered was linear and proportional to the number of cigarettes smoked onto one trap, up to about five cigarettes. After that point, the recovery leveled off, indicating consistent recovery of the carbonyls for no more than five cigarettes per trap. The level chosen for this work was three cigarettes per trap.

Elution of carbonyls from the silica gel trap. Two approaches were investigated: elution with solvent through the silica gel column, *versus* extraction by slurrying the gel in solvent. It was found that the elution technique removed virtually all of the carbonyls of interest while the slurry technique did not. This was determined using a standard acrolein solution and derivatizing following either elution or slurrying. Comparisons were then made to the same derivative prepared by treating the standard solution directly.

Choice of eluting solvent. The most convenient method would be to perform the derivatization in the eluting solvent itself; this limited the choice to either methanol or water, with subsequent isolation of derivatives by either evaporation or extraction. Both solvents eluted the carbonyls equally well, but elution with water was chosen because the subsequent extraction with ether introduced a useful clean-up step, in that the unreacted reagent could be held in the aqueous phase simply by acidifying before extraction.

Volume of eluting solvent. A 15-ml volume of water was found to be sufficient for complete elution of the carbonyls of interest. Increasing the volume to 40 ml made no difference in the results, and no attempt was made to decrease the volume below 15 ml.

Problems with quantitation

One difficulty with this method was that the most prevalent carbonyl in cigarette smoke, acetaldehyde, could not be determined. For some as yet unexplained reasons, peaks corresponding to the benzyloxime derivative of acetaldehyde appear in the reagent blanks of the respective preparations. Mass spectra of these peaks are identical to the spectra of the authentic acetaldehyde derivatives, but as stated, their source in the blanks is at present unknown.

Another problem encountered was the lack of reproducibility from run to run. Although the reproducibility of the GC step was very good (as measured by repeated injections of the same solution), a fairly wide range of values were obtained for some of the oximes following replicate analyses. For this reason, the method is described as semi-quantitative.

A third difficulty was that several of the carbonyls form two geometric isomers (*syn* and *anti*) of the oximes. This was not a major problem, since the ratio of major to minor peaks was found to be constant under a given set of conditions. Also, the only compounds for which the minor peak was substantial (*i.e.*, $>10\%$ of the major peak) were acetaldehyde and hexanal. As stated above, acetaldehyde could not be determined by this method, and hexanal is present in only very small amounts (if any) in the smoke of the cigarettes studied, and was in fact added as the internal standard.

The values obtained for the carbonyls conform reasonably well with the published figures[8–18]. One of the exceptions is acrolein for which the values are significantly lower than has been generally reported.

CONCLUSIONS

Described is a procedure for the collection of low-molecular-weight carbonyls from cigarette whole smoke, and the subsequent separation of their benzyloxime derivatives by glass-capillary GC. In addition, the use of a nitrogen selective detector

results in enhancement of sensitivity and considerable simplification of the chromatogram.

The utility of the procedure described in this paper lies in the fact that good separation of many carbonyls found in cigarette smoke is achieved chromatographically, thus making possible the generation of useful qualitative and semi-quantitative information about this very important class of compounds in cigarette smoke, or in other complex matrices.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance and advice of Duane Watson, and the help given by Beverly Wood, a summer intern, who performed much of the derivatization and chromatographic work. Acknowledgement is also made of John Bivins for the fabrication of the smoke absorption traps, and of Frank Hatch for the gas chromatography–mass spectrometry work.

The previous work of Robert Esperdy with silica gel as a trapping medium for smoke was also very helpful.

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