ANALYSIS OF LIQUID ODORANTS BY GAS CHROMATOGRAPHY

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INTRODUCTION

Before the introduction of gas chromatography, the analysis of odorants was a tedious undertaking. Usually, the odorant was carefully fractionated by distillation and each cut analyzed by physical and chemical means. However, with the aid of gas chromatography, commercial odorants and odorant mixtures may now be analyzed quickly and accurately. This paper compares an isothermal method used successfully for several years in analyzing commercial odorants with a recently developed programmed temperature method which is particularly helpful in analyzing blends with wide boiling ranges. Area response factors were determined for the compounds encountered in odorants, and the accuracy of the isothermal and programmed temperature methods were evaluated. Previous methods have not reported response factors for these compounds[1-7].

ISOTHERMAL METHOD

Experimental procedure

A Perkin-Elmer Model 154B Vapor Fractometer with a thermistor detector is used. The column is 7 ft. by 1/4-in. O.D. aluminum tubing containing 3.5 ± 0.1 g packing per ft. of 42–60 mesh Johns-Manville GC-22 insulating firebrick impregnated with 28.6 wt. % didecyl phthalate. Helium is used as the carrier gas at a flow rate of 60 ml/min measured at 25° and atmospheric pressure. Column inlet pressure is 6.5 p.s.i.g., column temperature is 50°, and sample size is approximately 0.01 ml. In order to make sure that the whole sample is accounted for, the carrier gas flow is reversed at the end of the time allotted for forward flow, and the detector is switched to the column inlet. The time of this backflush is usually 10 min longer than that allowed for forward flow. The backflush should be negligible for a satisfactory analysis.

Retention data

Fig. 1 is a typical chromatogram of a mixture of mercaptans. The *n*-amyl mercaptan is accounted for as a backflush peak in this analysis to illustrate the backflush technique. As expected, this peak is quite wide. In the analysis of the sulfide blend shown in Fig. 2, the forward flow was continued until the highest boiling compound (thiophan) present in the blend was eluted.

Fig. 3 shows the retention time as a function of boiling point for both mercaptans and sulfides. Although didecyl phthalate is somewhat polar, a single straight line correlation is obtained. More polar columns would yield two lines, one for mercaptans and one for sulfides. The single correlation allows easy identification of unknown

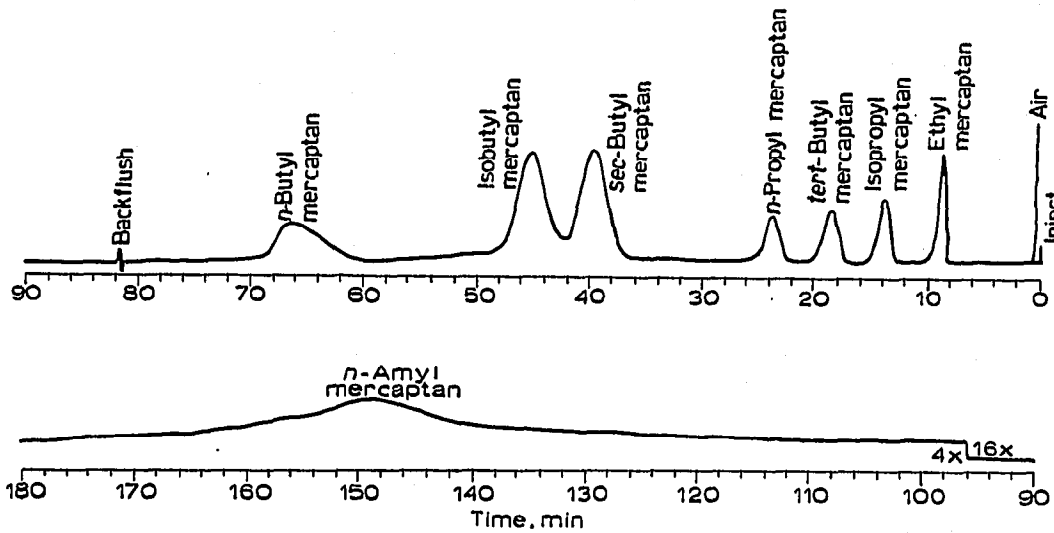

Fig. 1. Isothermal chromatogram of mercaptan blend.

mercaptans and sulfides. The separation of *n*-propyl mercaptan and methyl ethyl sulfide is not complete. However, this is not serious because methyl ethyl sulfide is not normally present in odorants.

Response factors

Relative weight correction factors are normally used in gas chromatographic calculations to convert area per cent to weight per cent. This corrects for variation in detector response of the individual components. The correction is made by multiplying the area of each peak by the respective correction factor. The factors for mercaptans and sulfides were determined by analyzing blends containing known amounts of mercaptans and sulfides with a known amount of *n*-heptane. The weight correction factor for a component relative to that of benzene is calculated by:

$$f_C = \frac{A_H}{A_C} \times \frac{W_C}{W_H} \times f_H$$

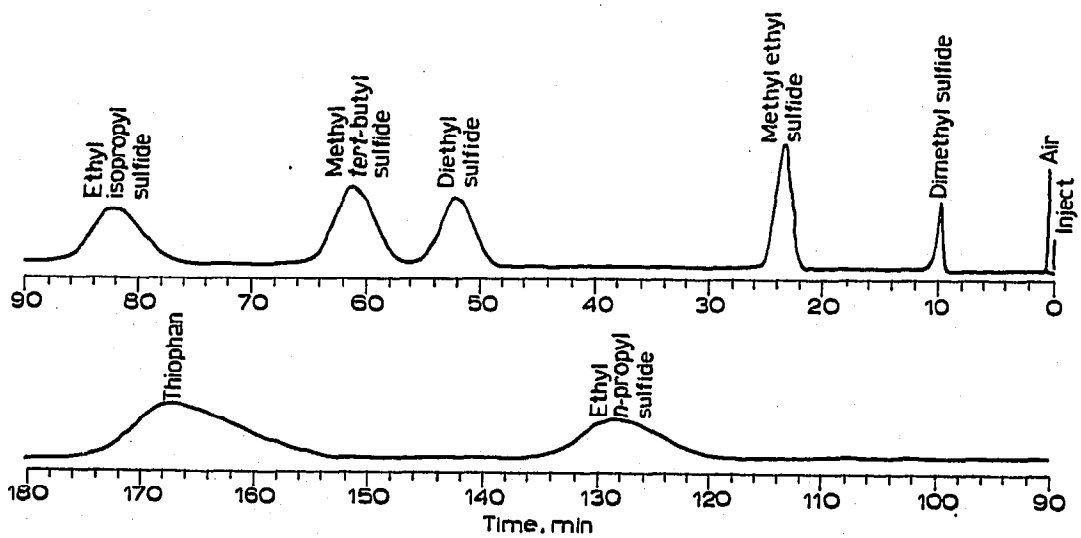

Fig. 2. Isothermal chromatogram of sulfide blend.

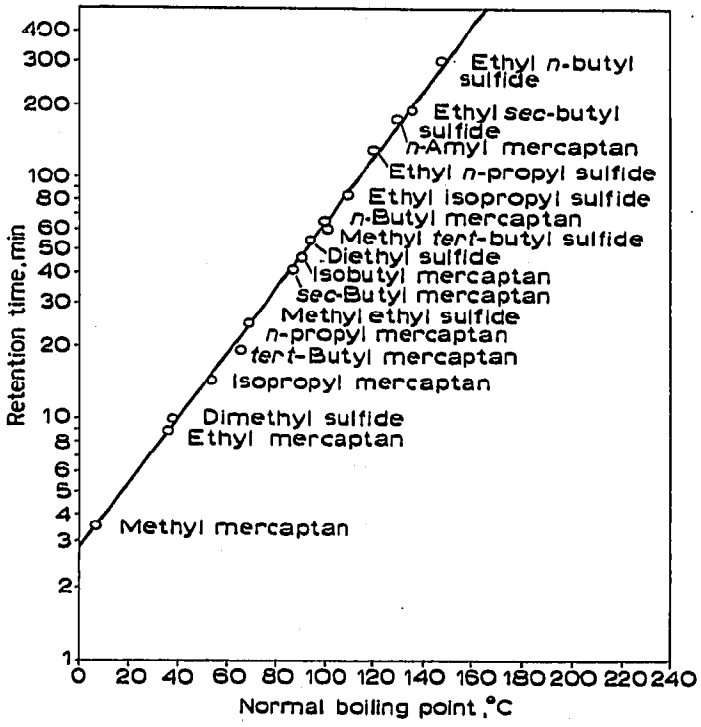

Fig. 3. Correlation of retention time with boiling point for mercaptans and sulfides.

where A_H and A_C are the areas of the *n*-heptane and the component, W_H and W_C are the weights of the *n*-heptane and the component, and f_H (= 0.898) is the weight correction factor of *n*-heptane relative to benzene (f = 1.00). Weight correction factors for mercaptans and sulfides are shown in Table I. The values tend to increase with molecular weight and are quite different for the mercaptans and sulfides. Failure to use these correction factors in the analysis of odorants would lead to error.

TABLE I

WEIGHT CORRECTION FACTORS

Compound	*Isothermal*	*Programmed temperature*	*Average*
Ethyl mercaptan	1.42	1.42	1.42
Isopropyl mercaptan	1.60	1.59	1.59
tert.-Butyl mercaptan	1.64	1.67	1.65
n-Propyl mercaptan	1.48	1.50	1.49
sec.-Butyl mercaptan	1.64	1.58	1.61
Isobutyl mercaptan	1.58	1.63	1.61
n-Butyl mercaptan	1.70	1.62	1.66
n-Amyl mercaptan	2.02	2.03	2.03
Dimethyl sulfide	0.91	0.94	0.92
Methyl ethyl sulfide	0.97	0.97	0.97
Diethyl sulfide	0.96	0.96	0.96
Methyl *tert.*-butyl sulfide	1.10	1.10	1.10
Ethyl isopropyl sulfide	1.05	1.07	1.06
Ethyl *n*-propyl sulfide	1.22	1.21	1.22
Thiophan	1.08	1.04	1.06

Molar response factors

Molar response factors relative to benzene (= 100) are related to weight correction factors by:

$$\text{Molar response factor} = \frac{\text{molecular weight}}{\text{weight correction factor}} \times \frac{100}{78}$$

(78 = molecular weight of benzene).

MESSNER *et al.*, obtained a linear relationship between molar response and molecular weight for several homologous series[8]. However, molar response factors calculated from the average relative weight correction factors in Table I and plotted *vs.* boiling point in Fig. 4 show a decrease in response factors at high molecular weights. This

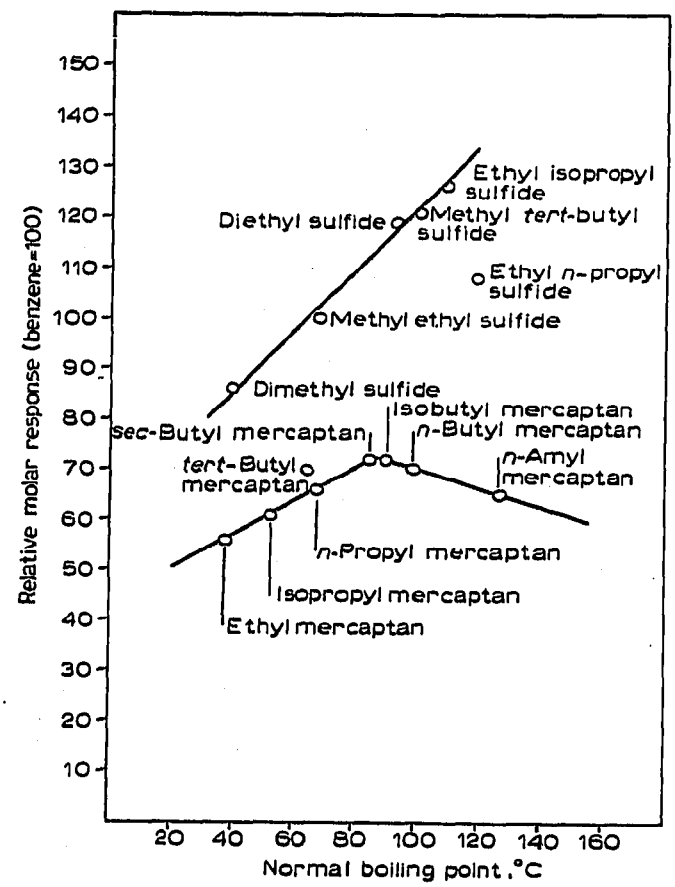

Fig. 4. Correlation of molar response factors with boiling point for mercaptans and sulfides at 50°.

decrease was observed in repeated measurements. Although the reason for this decrease in molar response factor is not known, it has been observed with other substances and is always associated with high boiling and/or high molecular weight substances.

Quantitative results

Three runs were made on each of the blends of mercaptans and sulfides shown in Figs. 1 and 2, and the experimental compositions were calculated using the area correction factors in Table I. Good agreements were obtained with actual compositions as is seen in Tables II and III.

TABLE II

ANALYSIS OF MERCAPTAN BLEND BY ISOTHERMAL METHOD

Component	Composition, wt. %				Standard deviation
	Actual	Run 1	Run 2	Run 3	
Ethyl mercaptan	10.7	11.0	10.8	10.7	0.2
Isopropyl mercaptan	10.8	10.8	10.8	11.0	0.1
n-Propyl mercaptan	11.2	11.7	11.3	11.4	0.3
tert.-Butyl mercaptan	12.2	12.5	12.6	12.3	0.3
sec.-Butyl mercaptan	11.3	11.6	11.2	11.0	0.3
Isobutyl mercaptan	11.8	11.9	12.4	12.1	0.4
n-Butyl mercaptan	29.5	29.4	28.7	29.3	0.5
n-Amyl mercaptan	2.5	1.1	2.2	2.2	0.8

TABLE III

ANALYSIS OF SULFIDE BLEND BY ISOTHERMAL METHOD

Component	Composition, wt. %				Standard deviation
	Actual	Run 4	Run 5	Run 6	
Dimethyl sulfide	8.6	8.6	9.0	8.6	0.2
Methyl ethyl sulfide	8.6	8.6	8.8	8.6	0.1
Diethyl sulfide	10.0	10.0	10.2	9.9	0.1
Methyl *tert.*-butyl sulfide	15.4	15.4	15.7	15.2	0.2
Ethyl isopropyl sulfide	12.6	12.7	12.8	12.8	0.2
Ethyl *n*-propyl sulfide	16.4	16.7	16.4	16.3	0.2
Thiophan	28.3	27.9	27.2	28.5	0.7

PROGRAMMED TEMPERATURE METHOD

Experimental procedure

Although isothermal operation gives a satisfactory analysis for most odorants, programmed temperature operation decreases the analysis time and eliminates backflushing of the higher boiling compounds. A 24-ft. by 1/4-in. O.D. stainless steel column containing 2.3 $\pm$ 0.2 g packing per ft. of 60–80 mesh Johns-Manville Silicone Treated Chromosorb W impregnated with 28.6% didecyl phthalate is used in the programmed temperature method. The column is programmed from 35–180° at 2°/min. The retention temperature is measured with a thermocouple placed inside the column at the exit. The helium flow rate is 75 ml/min measured at 25° and atmospheric pressure, and the column inlet pressure varies from 31–53 p.s.i.g. over the temperature range. A high resistance tungsten thermal conductivity detector is used and operated at 150°. Sample size is approximately 0.04 ml. A single-column unit constructed at Calresearch was used for the analysis reported here.

Retention time data

Chromatograms of mercaptans and sulfides analyzed by the programmed temperature procedure are shown in Figs. 5 and 6. Comparison with the isothermal chromatograms of the identical samples in Figs. 1 and 2 illustrates the savings in time which can be realized by programmed temperature operation. The resolution is greater due to the

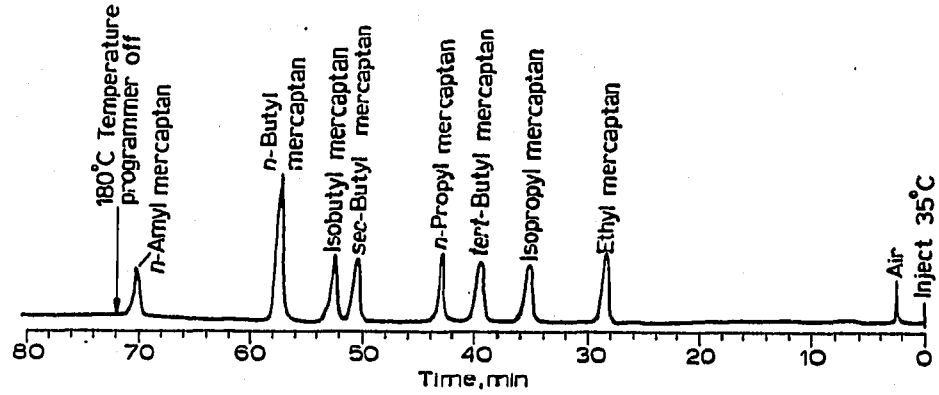

Fig. 5. Programmed temperature chromatogram of mercaptan blend.

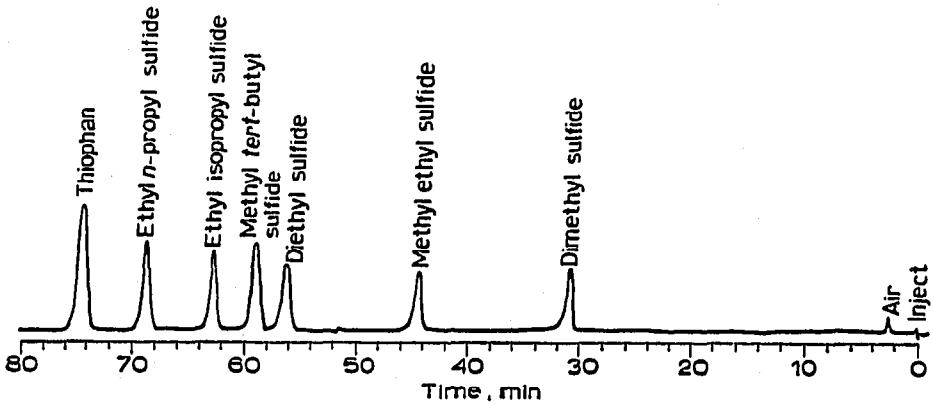

Fig. 6. Programmed temperature chromatogram of sulfide blend.

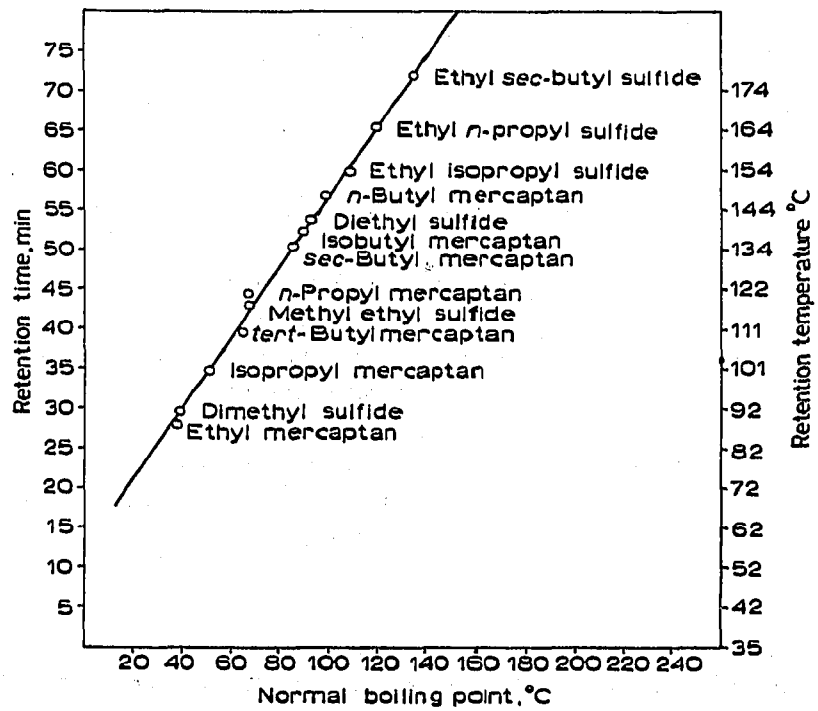

Fig. 7. Correlation of retention time and retention temperature with boiling point for mercaptans and sulfides under programmed temperature operation.

increased column length. In addition, the peaks are all evenly spaced which avoids crowding in the front and large voids toward the end of the chromatogram. In linear programmed temperature gas chromatography, the retention time is directly proportional to the boiling point for homologous series, whereas, in isothermal gas chromatography the logarithm of the retention time is proportional to the boiling point. As with the logarithmic plot of retention times shown in Fig. 3, a single boiling point correlation of all the mercaptans and sulfides is obtained in Fig. 7 regardless of the branching. The right-hand ordinate shows the retention temperature at which the compounds elute from the column. The departure from linearity of the temperature scale is due to a slight lag in the column temperature during programming.

Response factors

Weight correction factors were measured for the programmed method in the same manner as in the isothermal method. Within the limits of measurement, identical values are obtained as seen in Table I. This illustrates that relative correction factors are independent of flow rate, temperature, concentration, and type of thermal conductivity detector.

Quantitative results

Three analyses were made on each of the mercaptan and sulfide blends analyzed by the isothermal method. Standard deviations from actual compositions are, in general, slightly higher for the programmed method. However, the agreements are still quite good as seen in Tables IV and V.

TABLE IV

ANALYSIS OF MERCAPTAN BLEND BY PROGRAMMED TEMPERATURE METHOD

Component	Composition, wt. %				Standard deviation
	Actual	Run 1	Run 2	Run 3	
Ethyl mercaptan	10.7	11.1	10.7	12.5	1.1
Isopropyl mercaptan	10.8	10.8	10.5	9.9	0.5
n-Propyl mercaptan	11.2	11.5	10.7	10.6	0.5
tert.-Butyl mercaptan	12.2	12.1	11.5	11.5	0.6
sec.-Butyl mercaptan	11.3	11.8	12.2	11.3	0.6
Isobutyl mercaptan	11.8	11.3	11.9	12.1	0.3
n-Butyl mercaptan	29.5	29.0	30.1	29.8	0.5
n-Amyl mercaptan	2.5	2.4	2.4	2.3	0.1

TABLE V

ANALYSIS OF SULFIDE BLEND BY PROGRAMMED TEMPERATURE METHOD

Component	Composition, wt. %				Standard deviation
	Actual	Run 4	Run 5	Run 6	
Dimethyl sulfide	8.6	8.3	8.5	9.3	0.4
Methyl ethyl sulfide	8.6	8.6	8.2	8.8	0.3
Diethyl sulfide	10.0	10.2	9.9	9.7	0.2
Methyl *tert.*-butyl sulfide	15.4	15.7	15.0	15.4	0.3
Ethyl isopropyl sulfide	12.6	12.3	12.6	12.3	0.2
Ethyl *n*-propyl sulfide	16.4	17.0	16.2	16.0	0.4
Thiophan	28.3	28.0	29.6	28.6	0.8

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SUMMARY

Isothermal and programmed temperature methods for gas chromatographic analysis of mercaptans and sulfides used in odorants are discussed. Relative retention times and compound response factors are summarized. Chromatograms of known mixtures are shown. Average standard deviations from actual concentrations are 0.3% for the isothermal method and 0.5% for the programmed method.

REFERENCES

1 D. F. ADAMS AND R. K. KOPPE, *Tappi*, 42 (7) (1959) 601.
2 C. H. AMBERG, *Can. J. Chem.*, 36 (1958) 590.
3 H. J. COLEMAN, C. J. THOMPSON, C. C. WARD AND H. T. RALL, *Anal. Chem.*, 30 (1958) 1592.
4 J. H. KARCHMER, *Anal. Chem.*, 31 (1959) 1377.
5 S. A. RYCE AND W. A. BRYCE, *Anal. Chem.*, 29 (1957) 925.
6 C. F. SPENCER, F. BAUMANN AND J. F. JOHNSON, *Anal. Chem.*, 30 (1958) 1473.
7 J. H. SULLIVAN, J. T. WALSH AND C. MERRITT, *Anal. Chem.*, 31 (1959) 1826.
8 A. E. MESSNER, D. M. ROSIE AND P. A. ARGABRIGHT, *Anal. Chem.*, 31 (1959) 230.