Results and discussion

Fig. 1 shows the chromatogram of a mixture of standard amino acids and tyramine, 1 μmole of each. Constants calculated (for 1 μmole) by the method of SPACKMAN *et al.*[2] are as follows: ammonia 19.2, lysine 22.1, histidine 18.6, arginine 18.5, tyramine 17.0. Excluding tyramine which cannot be determined on IR-120 resin, these compounds are determined as accurately (*i.e.* equal linearity and sensitivity) off CG-50 columns as off the regular IR-120 resin. The linearity of tyramine in the range 0.25 to 2.0 μmoles is shown in Fig. 2. Analyses of 10 standard samples on the same column resulted in a tyramine constant of 17.0 ± 0.3, indicating a reproducibility of better than 2 %.

Our early efforts to modify the procedure of MOORE, SPACKMAN AND STEIN[1] by changing the temperature, column length, flow rate and pH of the buffer did not improve the results for tyramine. Combining certain features of the method of KIRSHNER AND GOODALL[3] with those of the above method, however, has resulted in a relatively rapid technique for the quantitative determination of tyramine together with ammonia, lysine, histidine and arginine. Application of this procedure required only two changes in the normal operation of the Beckman/Spinco amino acid analyzer: (a) the use of CG-50 resin in place of IR-120 resin and (b) a column temperature of 63° instead of 50°. We have used this technique for the analysis of acidified (0.1 *N* HCl) 80 % ethanol extracts of banana plant tissues which were concentrated to remove ethanol, adjusted between pH 3 and 5.5, and brought to volume with water. When standard amounts of tyramine were added during the homogenization of the tissue, recoveries of tyramine were 96 ± 3 %. No regeneration of the column was necessary. However, the top few centimeters of resin were replaced after each analysis if the plant extracts contained appreciable amounts of tannins and pigments. When an analysis of tyramine alone was desired, changes in column length to 10 cm and temperature to 25° permitted a complete quantitative determination in less than 2 h.

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[1] S. MOORE, D. H. SPACKMAN AND W. H. STEIN, *Anal. Chem.*, 30 (1958) 1185.
[2] D. H. SPACKMAN, W. H. STEIN AND S. MOORE, *Anal. Chem.*, 30 (1958) 1190.
[3] N. KIRSHNER AND MCC. GOODALL, *J. Biol. Chem.*, 226 (1957) 207.
[4] T. L. PERRY AND W. A. SCHROEDER, *J. Chromatog.*, 12 (1963) 358.
[5] C. H. W. HIRS, S. MOORE AND W. H. STEIN, *J. Biol. Chem.*, 200 (1953) 493.

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Relative detector response in gas chromatography

V. Halogenoalkanes, aliphatic aldehydes, pyridines

The investigation of the relative detector response of a thermal conductivity detector to organic compounds of various types, when nitrogen is the carrier gas, is continued with a study of relative responses to members of the homologous series halogenoalkanes, aliphatic aldehydes and pyridines.

TABLE I

RELATIVE DETECTOR RESPONSES TO SOME HALOGENOALKANES, ALIPHATIC ALDEHYDES AND PYRIDINES

Compound	*Mol. wt.*	*Response per mole relative to benzene (= 100)*
Halogenoalkanes		
1-Chloropropane	78.7	90
1-Chlorobutane	92.7	114
2-Chlorobutane		103
1-Chloropentane	106.7	138
1-Chloro-3-methylbutane		129
2-Chloro-3-methylbutane		111
1-Chlorohexane	120.7	162
1-Chloroheptane	134.7	185
1-Bromopropane	123	132
2-Bromopropane		121
1-Bromobutane	137	162
2-Bromobutane		149
2-Bromo-2-methylpropane		131
1-Bromopentane	151	186
1-Bromo-3-methylbutane		173
2-Bromopentane		166
1-Bromohexane	165	210
Iodoethane	156	162
1-Iodopropane	170	187
2-Iodopropane		173
1-Iodobutane	184	211
1-Iodo-2-methylpropane		197
2-Iodobutane		194
1-Iodopentane	198	236
1-Iodohexane	212	259
Aliphatic aldehydes		
Butanal	72	66
Pentanal	86	88
Hexanal	100	108
Heptanal	114	128
Octanal	128	151
Decanal	156	189
Pyridines		
Pyridine	79	100
2-Methylpyridine	93	126
3-Methylpyridine		125
4-Methylpyridine		127
2-Ethylpyridine	107	148
4-Ethylpyridine		146
2,5-Dimethylpyridine		147
2,6-Dimethylpyridine		144
3,4-Dimethylpyridine		131
3,5-Dimethylpyridine		144
4-(*n*-Propyl)-pyridine	121	166
2,4,6-Trimethylpyridine		169
Piperidine	85	95

Experimental

Gas–liquid chromatography was carried out using the apparatus described previously[1]. Nitrogen was used as the carrier gas at a flow rate of approximately 33 ml/min, and the bridge current was 100 mA. Under the conditions used no reversal of peaks was observed for any of the compounds studied.

The compounds were obtained from commercial suppliers and most of them could be obtained chromatographically pure by fractional distillation. In those instances when more than one peak was obtained from a compound even after repeated fractionation, that compound was purified by using a preparative chromatographic apparatus.

Results and discussion

The relative detector responses to a number of halogenoalkanes, aliphatic aldehydes and pyridines are shown in Table I.

An examination of these results shows that there is, in each homologous series, an increase in relative detector response with an increase in molecular weight. The increment for each CH_2 group is approximately 24 units of response for chloroalkanes, 26 units for bromoalkanes, 24 units for iodoalkanes, 20 units for aliphatic aldehydes and 23 units for pyridines. These increments are similar to those found for other homologous series[2,3].

It is also found that, in the halogenoalkanes, there is a decrease in relative response to isomeric compounds with an increase in chain branching. This decrease in relative response is similar to that found previously for isomeric alkyl benzenes[4], aliphatic esters[5] and aliphatic ethers[2].

In the pyridine series it is found that, *ortho*-effects and chain-branching effects being absent, a compound with a group forming part of a side-chain has a similar relative detector response to the isomeric compound which has the group attached to the pyridine ring. In this respect the pyridine series resembles the benzene series[4].

No *ortho*-effect is observed for the monomethylpyridines but the relative response to 3,4-dimethylpyridine is lower than the responses to 2,5-, 2,6-, and 3,5-dimethylpyridines, which are similar.

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[1] G. R. JAMIESON, *J. Chromatog.*, 3 (1960) 464.
[2] G. R. JAMIESON, *J. Chromatog.*, 8 (1962) 544.
[3] G. R. JAMIESON, *Journées Internationales d'Etude des Méthodes Immédiate et de Chromatographie*, Gams, Paris, 1961, p. 85.
[4] G. R. JAMIESON, *J. Chromatog.*, 3 (1960) 494.
[5] G. R. JAMIESON, *J. Chromatog.*, 4 (1960) 420.

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