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Note

Identification of food thickeners by monitoring of their pyrolytic products

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The analysis of polysaccharides presents various problems, particularly when polysaccharides used as food additives are to be quantitatively analysed. The analytical methods previously used for the identification and quantification of food thickeners include hydrolysis of polysaccharides[1] and determination of different monosaccharides by gas chromatography (GC)[2–5] or gas chromatography combined with mass spectrometry (GC–MS)[2,6] (Table I).

TABLE I

FOOD THICKENERS STUDIED AND THEIR HYDROLYTIC PRODUCTS[1]

Polysaccharide	*Monomeric compounds and their molar relationships*
Guar	Mannose, galactose 2:1
Carob	Mannose, galactose 4:1
Tragacanth	Galacturonic acid, galactose, glucose, arabinose, xylose, fucose, rhamnose*
Gum arabic	Glucuronic acid, rhamnose, arabinose, galactose*
Alginate	Mannuronic acid, guluronic acid 1:0.48–1.85
Pectin	Galacturonic acid (some galactose, glucose, arabinose, rhamnose)
Carrageenan	Galactose, 3,6-anhydrogalactose, galactose sulphate*
Furcellaran	Galactose, 3,6-anhydrogalactose, galactose sulphate*
Carboxymethylcellulose	Glucose

* Varying molar relationships.

Alternatively, direct analysis by electrophoretic methods[7,8] can be used. However, there are difficulties in using cellulose acetate membranes[7] in the electrophoretic separation of the galactomannans, guar and carob because of their similar chemical composition.

Combined GC–gas-phase thermal fragmentation has been used for the identification of pyrolytic products from bark polysaccharides[9]. The formation of specific patterns of degradation products, and their relative amounts present in the pyrogram, has been found to provide information on the parent molecule.

In this work a method is described in which polysaccharides used as food

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additives were isolated and pyrolysed and the products of pyrolysis were analysed by GC. It was possible to identify a single food thickener by retention index monitoring (RIM) and selected ion monitoring (SIM) of its pyrolytic products, but accurate analysis of a mixture of food thickeners was not achieved by this method. Gravimetric determination of a precipitated thickener gave quantitative results.

EXPERIMENTAL

Standards

The food thickeners analysed as standards were gum guar, carob, tragacanth, gum arabic, alginic acid, pectin, carrageenan, furcellaran and carboxymethylcellulose, most of which were obtained from Sigma and Protan & Fagerton.

Isolation of polysaccharides

A sample of jam was homogenized and the polysaccharides were precipitated with ethanol. The precipitate was centrifuged, washed with ethanol and dried. The dried polysaccharides were dissolved in 0.067 *M* phosphate buffer of pH 7.2, and neutral and acid polysaccharides were separated on DEAE-cellulose[10]. The components were dialysed and dried before pyrolysis.

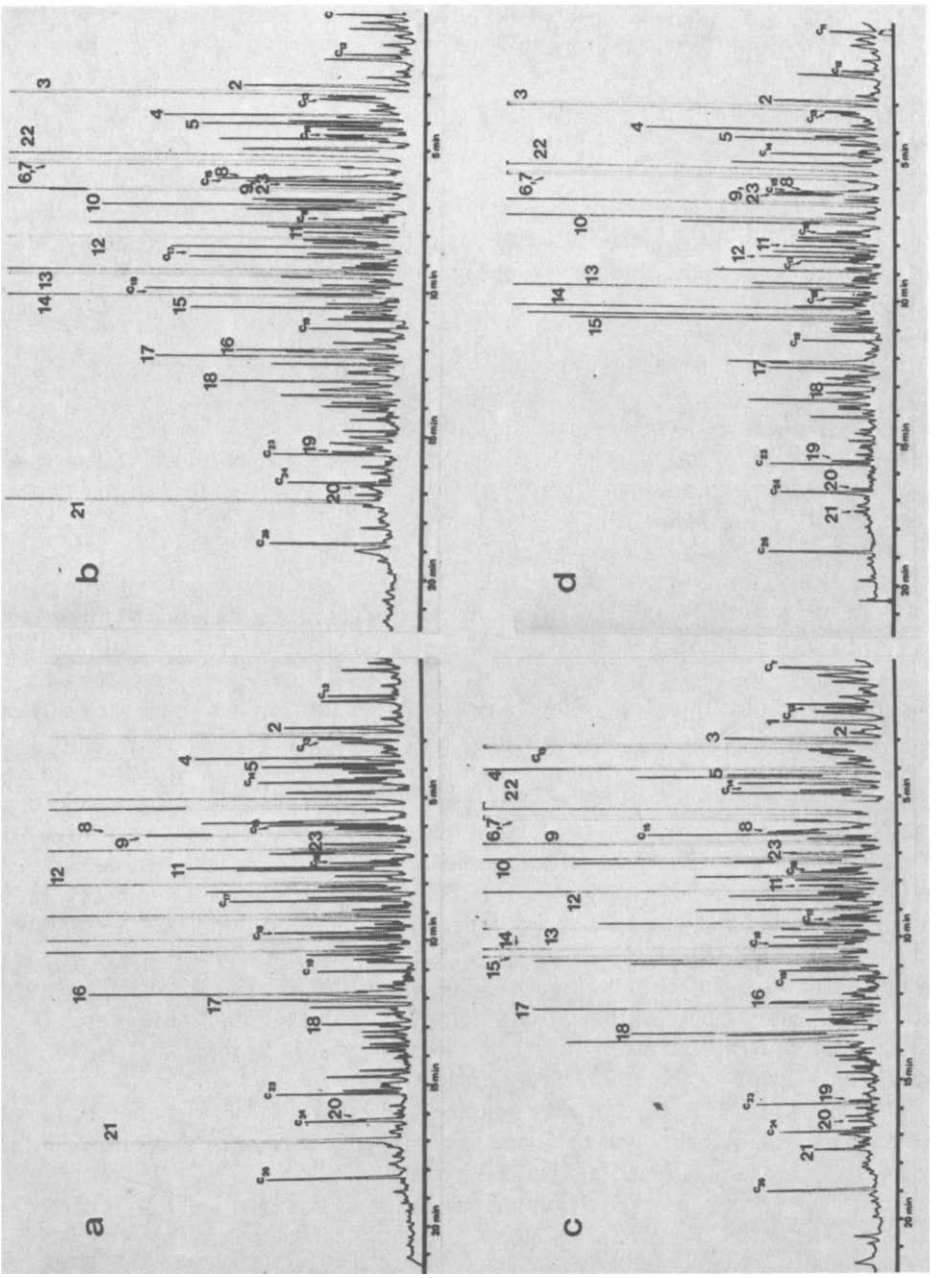
Pyrolysis and gas–liquid chromatography

A pyrolysator (190 Pyroprobe, Perkin-Elmer) was equipped with either a platinum plate or a platinum spiral with a quartz capillary tube. Polysaccharides were pyrolysed on the platinum plate or in the quartz tube, the optimum conditions for pyrolysis being 600°C and 20 sec (ramp 10°C/msec). The pyrolyses were carried out using 10–15 mg of a thickener, which was pyrolysed four to five times into a glass tube cooled to −20°C. The products of the pyrolyses were dissolved in 100 μl of diethyl ether, and 1 μl of this solution was injected into a gas–liquid chromatography (GLC) unit. It was also possible to pyrolyse a thickener directly into the injection device of a gas chromatograph for RIM analysis with the pyrolysator.

A Micromat HRGC 412 (Orion Analytica, Finland) gas chromatograph, equipped with an OV-351 fused-silica capillary column (20 m × 0.3 mm I.D.) and a flame ionization detector, was used. The operating conditions were as follows: linear temperature programming from 50 to 230°C at 10°C/min, helium as carrier gas (2.0 ml/min) and an injection volume of 1 μl. If possible, the pyrolyses were carried out in the injection device of the chromatograph, but, depending on the geometry of the GLC unit and on the sensitivity of the detector available, separate pyrolysis into a cooled test-tube was sometimes necessary.

A Micromat HRGC 412 was adapted for RIM. This included the use of C_{12}–C_{26} aliphatic hydrocarbons as internal reference compounds. Retention indices of 1200 to 2600 were assigned to these compounds.

The acids produced were chromatographed and identified without prior derivatization. The RIM identification included quantification of the identified compounds. Identification of polysaccharides could be carried out by using the pattern-recognition program available.


a
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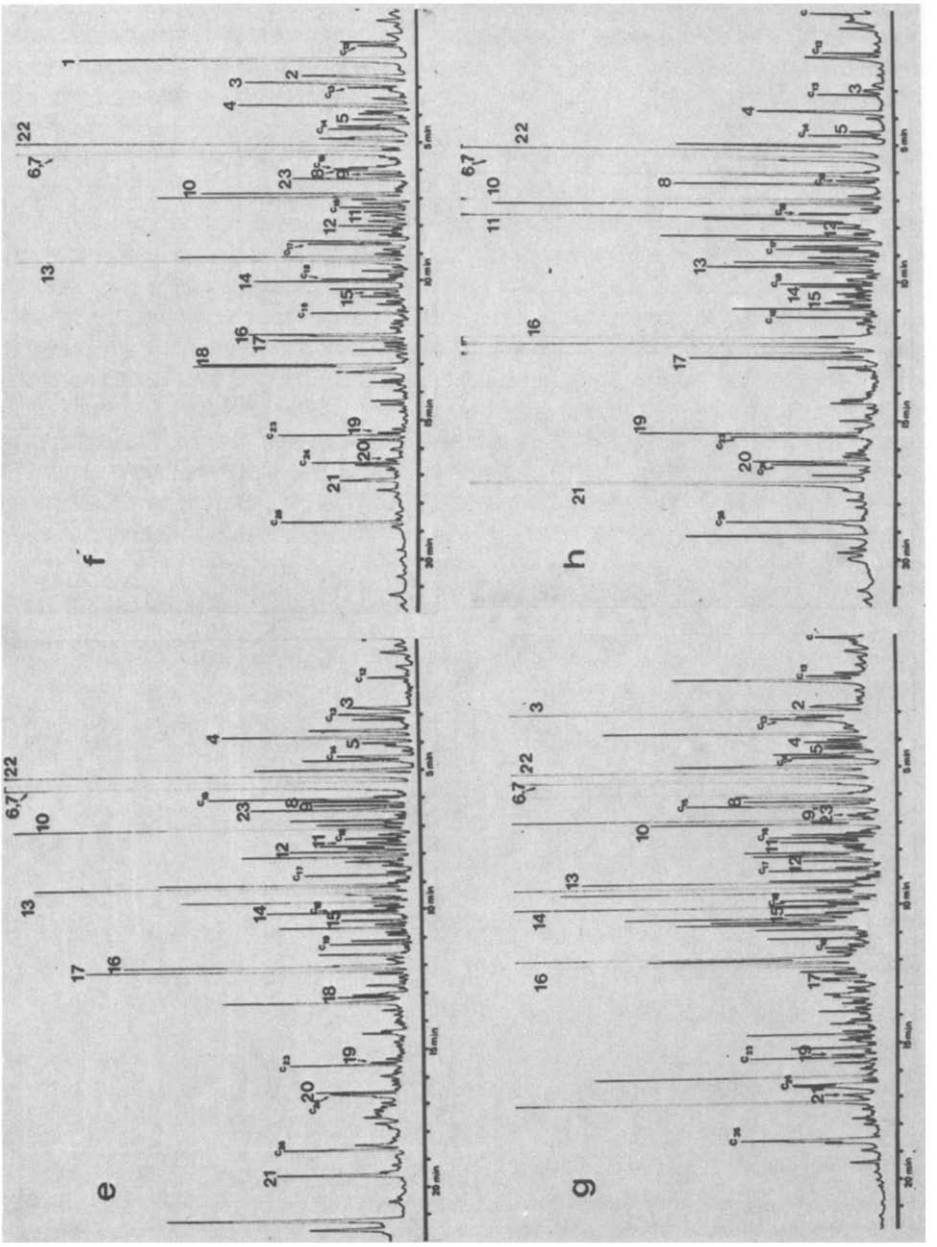

Fig. 1.

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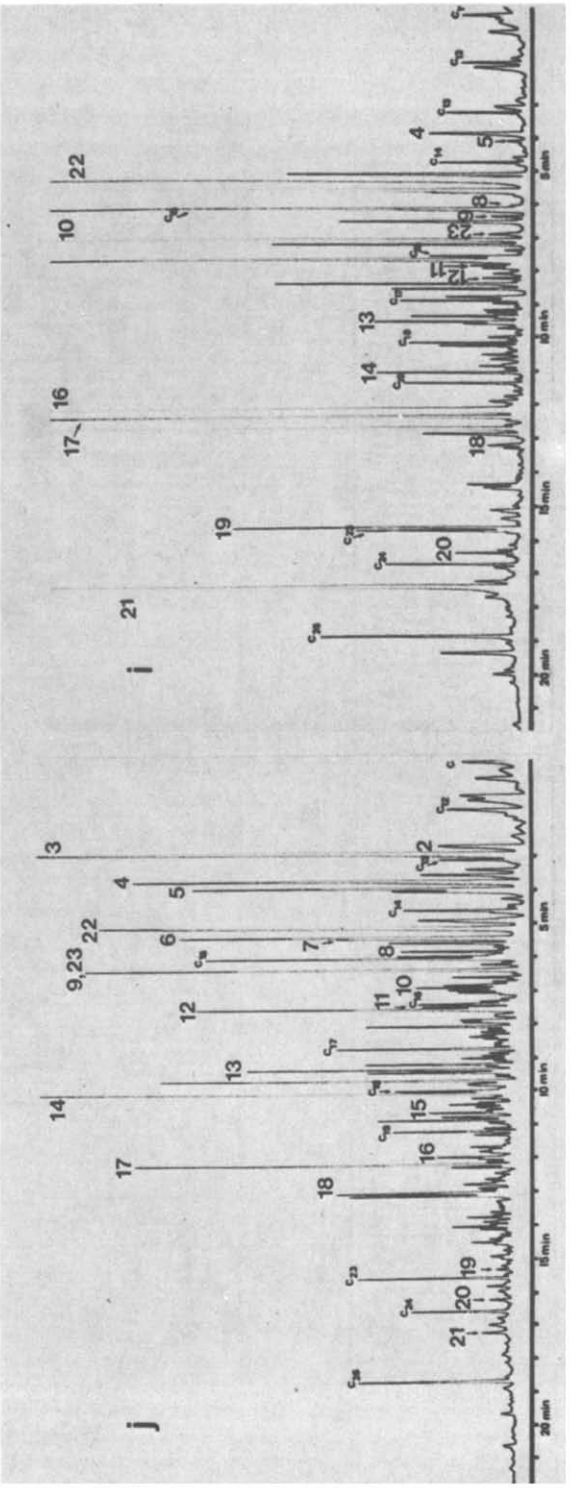

Fig. 1. Gas chromatograms (FID) of pyrolysis products of food thickeners. (a) Gum guar, (b) carob, (c) gum tragacanth, (d) gum arabic, (e) alginic acid, (f) pectin, (g), agar, (h) carrageenan, (i) furcellaran, (j) carboxymethylcellulose. The analyses were carried out using an OV-351 fused-silica column, 50–230°C, 10°C/min. C_{12}–C_{26} refer to internal standards.

GLC–MS

The qualitative identification of major volatile components of pyrolysis products was carried out by GLC–MS (70 eV, EJ) (Hewlett-Packard 5992 and 5997). The apparatus was equipped with an OV-351 fused-silica capillary column (25 m × 0.25 mm I.D.). The operating conditions were as follows: linear temperature programming from 50 to 230°C at 10°C/min, helium as carrier gas (2.0 ml/min) and an injection volume of 2 μl.

TABLE II

VOLATILE PYROLYTIC PRODUCTS OF FOOD THICKENERS AND THEIR RETENTION INDICES ANALYSED USING AN OV-351 WITH TEMPERATURE PROGRAMMING

	Gum guar	*Locust bean gum (carob)*	*Gum tragacanth*	*Gum arabic*	*Alginic acid*	*Pectin*	*Agar*	*Carrageenan*	*Furcellaran*	*Carboxymethylcellulose*	*Retention indices*
1 Acetic anhydride	–	–	+	–	–	+	–	–	–	–	1234
2 Acetoin	+	+	+	+	–	+	+	–	–	+	1271
3 Methyl formate	+	+	+	+	+	+	+	+	–	+	1285
4 3-Methylfurane	+	+	+	+	+	+	+	+	+	+	1343
5 2-Methyl-2-cyclopenten-1-one	+	+	+	+	+	+	+	+	+	+	1360
6 Furfural	+	+	+	+	+	+	+	+	+	+	1464
7 Acetylacetone	+	+	+	+	+	+	+	+	+	+	1463
8 2-Furylmethylketone	+	+	+	+	+	+	+	+	+	+	1500
9 2,4-Hexadienal	+	+	+	+	+	+	+	–	+	+	1509
10 5-Methyl-2-furfural	+	+	+	+	+	+	+	+	+	+	1561
11 Isomaltol	+	+	+	+	+	+	+	+	+	+	1620
12 2-Furanmethanol	+	+	+	+	+	+	+	+	+	+	1647
13 Cyclooctanone	+	+	+	+	+	+	+	+	+	+	1751
14 3-Methyl-2-hydroxycyclopentenone	+	+	+	+	+	+	+	+	+	+	1808
15 Hydroxyfuranone isomer	+	+	+	+	+	+	+	+	–	+	1839
16 Methyl-3-furanecarboxylate	+	+	+	–	+	+	+	+	+	+	1964
17 Phenol	+	+	+	+	+	+	+	+	+	+	1985
18 Benzyl alcohol derivative	+	+	+	+	+	+	–	–	+	+	2068
19 4-Oxopentanoic acid	–	+	+	+	+	+	+	+	+	+	2290
20 Furanecarboxylic acid derivative	+	+	+	+	+	+	–	+	+	+	2387
21 4-Methyl-4-hepten-3-one	+	+	+	+	+	+	+	+	+	+	2458
22 Acetic acid	+	+	+	+	+	+	+	+	+	+	–
23 Propionic acid	+	+	+	+	+	+	+	+	+	+	–
24 2-Methylpropionic acid	+	+	+	+	+	+	+	+	+	+	–
25 Butyric acid	+	+	+	+	+	+	+	+	+	+	–
26 3-Methylbutyric acid	+	+	+	+	+	+	+	+	+	+	–
27 Pentanoic acid	+	+	+	+	+	+	+	+	+	+	–
28 Hexanoic acid	+	+	+	+	+	+	+	+	+	+	–
29 Heptanoic acid	+	+	+	+	+	+	+	+	+	+	–
30 Octanoic acid	+	+	+	+	+	+	+	+	+	+	–
31 Nonanoic acid	+	+	+	+	+	+	+	+	+	+	–
32 Decanoic acid	+	+	+	+	+	+	+	+	+	+	–

Instead of flame ionization detection (FID) SIM, which had higher sensitivity and selectivity, could be adapted. Various ions were tested for their usefulness as indicators in the SIM analysis. The SIM of peaks at *m/e* 60 (acids), 88 (ethyl esters), 81 (furanes) and 95 (pyranes) and at *m/e* 108 and 126 were used to reveal differences between the tested polysaccharides.

RESULTS AND DISCUSSION

Gas chromatograms of the pyrolytic products are shown in Fig. 1 (a–j). Examination of 10 to 15 replicate pyrolyses revealed that the thickener standards gave reproducible pyrograms and that the peak-area ratios varied by $< 10\%$. Identified compounds as well as some preliminary identifications and their retention indices are presented in Table II. As can be seen in Fig. 1 (a–j) and Table II, the chromatograms had many similarities. Many of the identified compounds were present in all the pyrograms. However, some differences were also discernable. Because the pyrograms were reproducible. the differences in quantities of various monomeric compounds could be used in the identification of food thickeners.

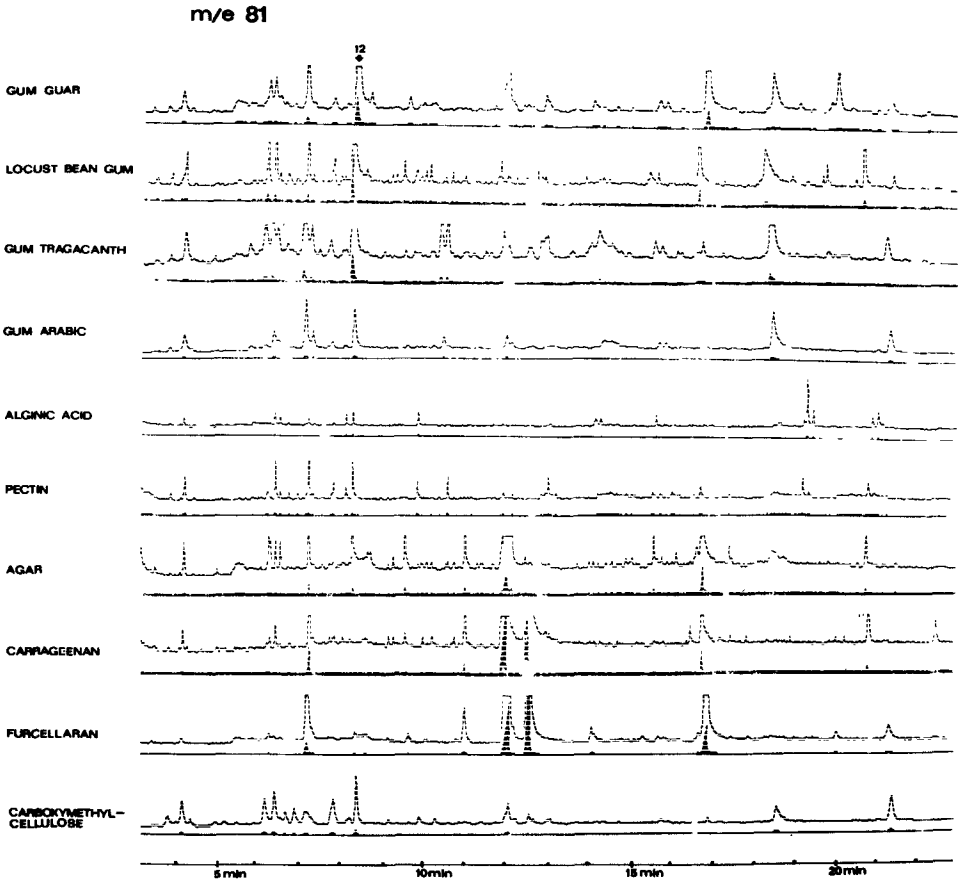

Fig. 2. Selected ion monitoring (*m/e* = 81) of the pyrolysis products of food thickeners analysed using an OV-351 fused-silica column, 50–230°C, 10°C/min.

The differences between the pyrograms could be observed more clearly by using the SIM technique as the detecting system for the pyrograms. Fig. 2 presents an example of SIM analysis (m/e = 81) of the pyrolytic products of the standard food thickeners used. An example of identifying the pyrolysis products of carboxymethylcellulose, isolated from a jam, with the aid of SIM with six ions is shown in Fig. 3.

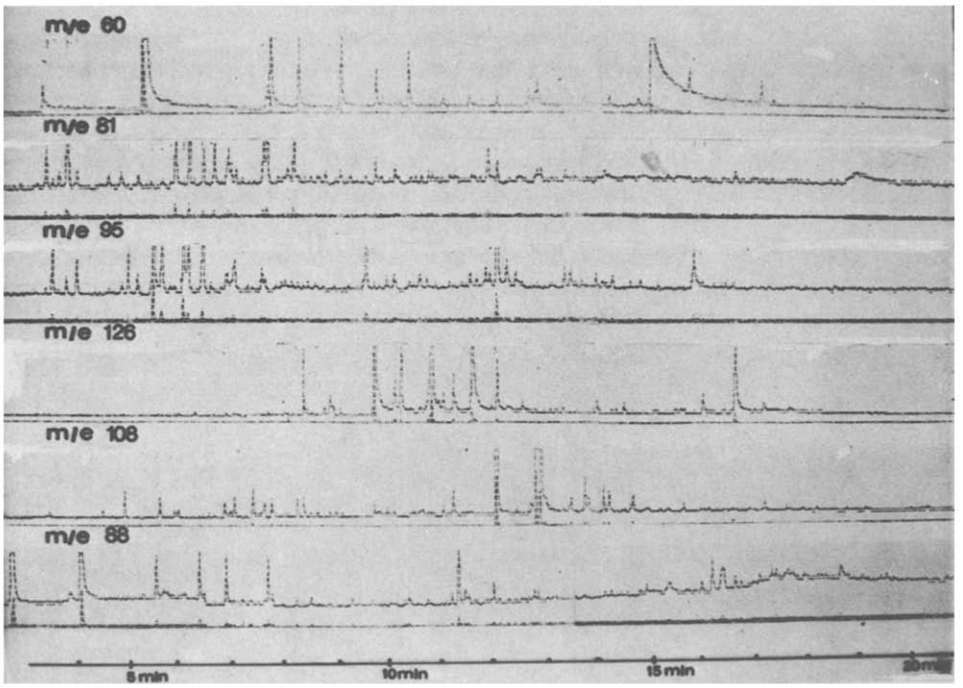

Fig. 3. Selected ion monitoring (m/e = 60, 81, 88, 95, 108 and 126) of the pyrolysis products of carboxymethylcellulose isolated from a jam.

This method is not universal, nor is it easy to use in routine quality-control analyses. In the case of mixtures, it may lead to too complicated pyrograms, and other methods such as electrophoresis may give further information. It is possible that a more highly developed method employing, *e.g.*, a dual-column and detector system could yield further information for the identification of food thickeners by monitoring of their pyrolysis products. However, the method described here is a new alternative for the analysis of polysaccharides used as food additives and can be used in conjunction with other methods.

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