Journal of Analytical and Applied Pyrolysis, 15 (1989) 159–165
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ANALYSIS OF CARAMEL COLOURS

CURIE-POINT PYROLYSIS–HIGH-RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND SIMULATION OF PYROLYSIS–MASS SPECTROMETRY

R. HARDT and W. BALTES *

Institut für Lebensmittelchemie, Technische Universität Berlin, Müller-Breslau-Strasse 10, D-1000 Berlin 12 (F.R.G.)

ABSTRACT

Curie-point pyrolysis–high-resolution gas chromatography/mass spectrometry enabled the differentiation of the four classes of caramel colours. The results of pyrolysis–mass spectrometry were simulated by data enhancement and addition of all spectra generated by pyrolysis–gas chromatography/mass spectrometry of a caramel colour. This method allowed the classification of unknown caramel colours with only few exceptions.

Caramel (colour); Curie-point pyrolysis; food colours; gas chromatography; mass spectrometry; pyrolysis.

INTRODUCTION

Caramel colours are brown food colourings, produced by heating sugars in the presence of browning accelerators. On the basis of the accelerators used, the following classes of caramel colours are recognised [1]:

Class I CP: Caramel Colour (Plain), Spirit Caramel
Class II CCS: Caramel Colour (Caustic Sulphite Process)
Class III AC: Ammonia Caramel Colour, Beer Caramel
Class IV SAC: Sulphite Ammonia Caramel, Soft Drink Caramel, Acid Proof Caramel

Nowadays gel filtration is mostly used for the detection of caramel colours in foodstuffs. This procedure, however, is not specific and therefore cannot be employed on food naturally containing brown compounds with high molecular weight.

0165-2370/89/$03.50

The aim of the present study was to investigate the extent to which Curie-point pyrolysis–high-resolution gas chromatography (HRGC)/mass spectrometry (MS) allowed the classification of an unknown caramel colour and the detection of these colourings in foodstuffs.

EXPERIMENTAL

Pyrolysis

Fischer Curie-Point Pyrolyzer Model 310. Pyrolysis temperature and time: 600 °C, 10 seconds. Sample amount: 100 μg.

Gas chromatography

Finnigan MAT 9610. Injector temperature: 250 °C. Split mode: splitless, after 1 min splitting ratio 1 : 5. Oven temperature programme: 40 °C for 5 min, 3 °C/min to 210 °C. Carrier gas: helium at a linear velocity of 35 cm/s. Capillary columns: J&W fused silica, (a) 30 m $\times$ 0.25 mm I.D., DB-210, 0.25 μm, (b) 30 m $\times$ 0.32 mm I.D., DB-210, 0.50 μm.

Mass spectrometry

Finnigan MAT 4500, INCOS data system. Ionization: electron impact, 70 eV. Ionizer temperature: 120 °C. Mass range: 35 to 300. Scan rate: 1 second, cyclic scan. GC/MS interface temperature: 230 °C.

CURIE-POINT PYROLYSIS–HRGC/MS

Fig. 1 shows typical pyrolysis–gas chromatograms of caramel colours (class I, III and IV, top to bottom). Important pyrolysis products are labelled with numbers. Their structural formulae and the most intensive m/z values in the mass spectra of these compounds are listed in Table 1. The pyrolysis–gas chromatogram of a caustic sulphite caramel colour and the mass fragmentogram of m/z 64 (SO_2, M^+) are presented in Fig. 2.

Sulphur dioxide is the main pyrolysis product of caramel colours of class II and IV. The pyrolyzates of caramel colours of class I, II and IV contain primarily furans and furanones, while nitrogen-containing heterocyclic compounds (especially pyrazines) dominate the pyrograms of ammonia caramel colours. These compounds can also be found in lower amounts in the pyrolyzates of sulphite ammonia caramels. Their main precursors seem to be

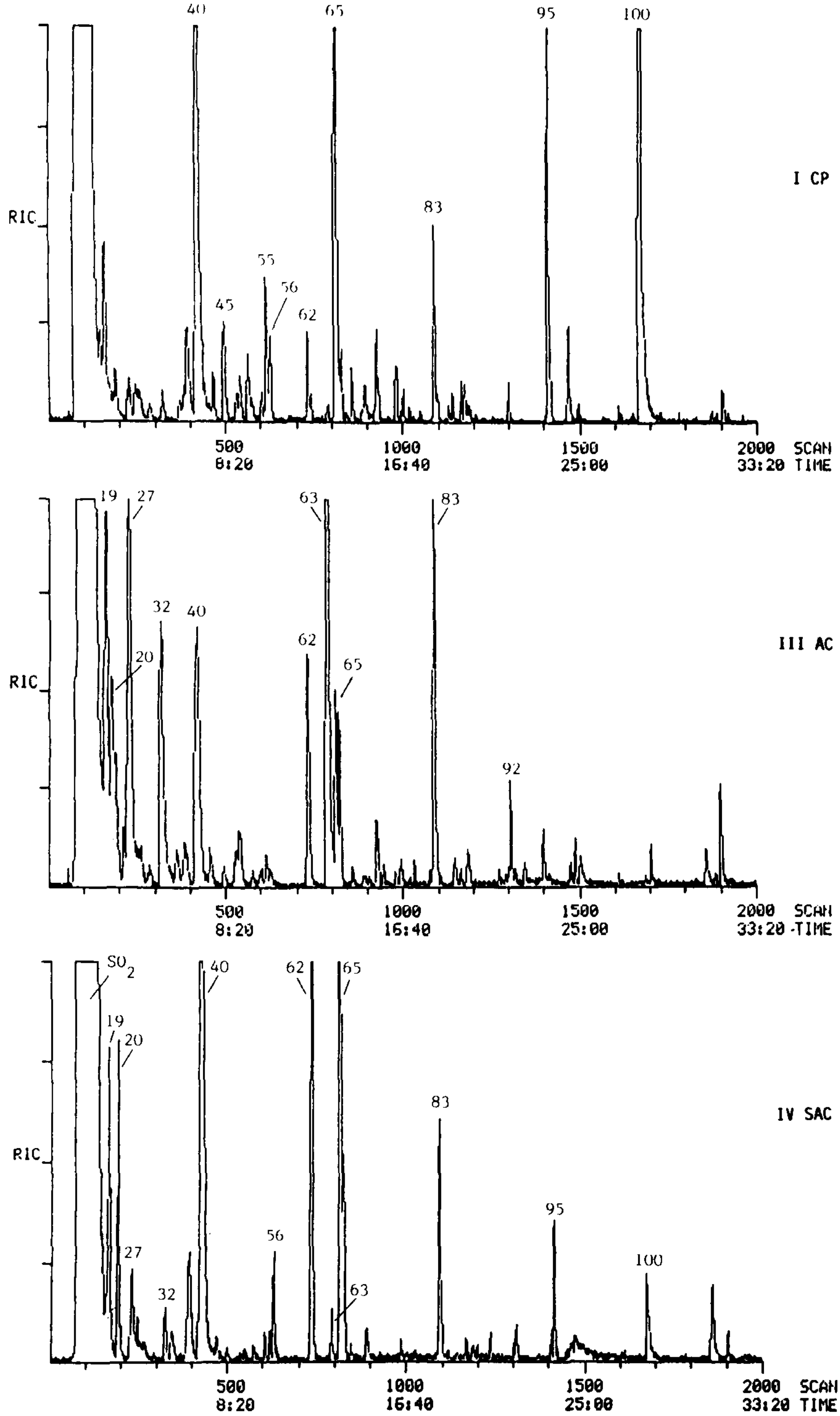
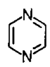
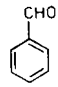
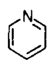
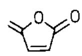
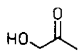
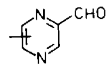
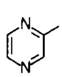
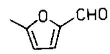
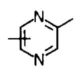
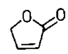
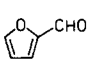
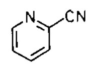
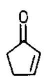
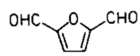
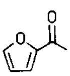
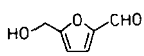


Fig. 1. Typical pyrolysis–gas chromatograms of caramel colours, class I, III and IV (top to bottom); capillary column (a).

TABLE 1

Main pyrolysis products

No.	Formula	m/z	No.	Formula	m/z
19		80, 53	56		77, 106, 105
20		79, 52	62		96, 68
23		74	63		122, 94
27		94, 67	65		110, 109
32		108	83		55, 84
40		96, 95	92		104, 77
45		82	95		124, 123
55		95, 110	100		97, 126

polyhydroxyalkylpyrazines, which are ingredients of ammonia and sulphite ammonia caramels [2].

Curie-point pyrolysis–HRGC/MS allows differentiation between the four classes of caramel colours on the basis of their pyrolysis products [3]. This method enables the detection of these colourings in liquid foodstuffs [4].

SIMULATION OF PYROLYSIS–MS

Because of the qualitative differences in their pyrolyzates the classification of caramel colours should also be possible by pyrolysis–MS. Using the

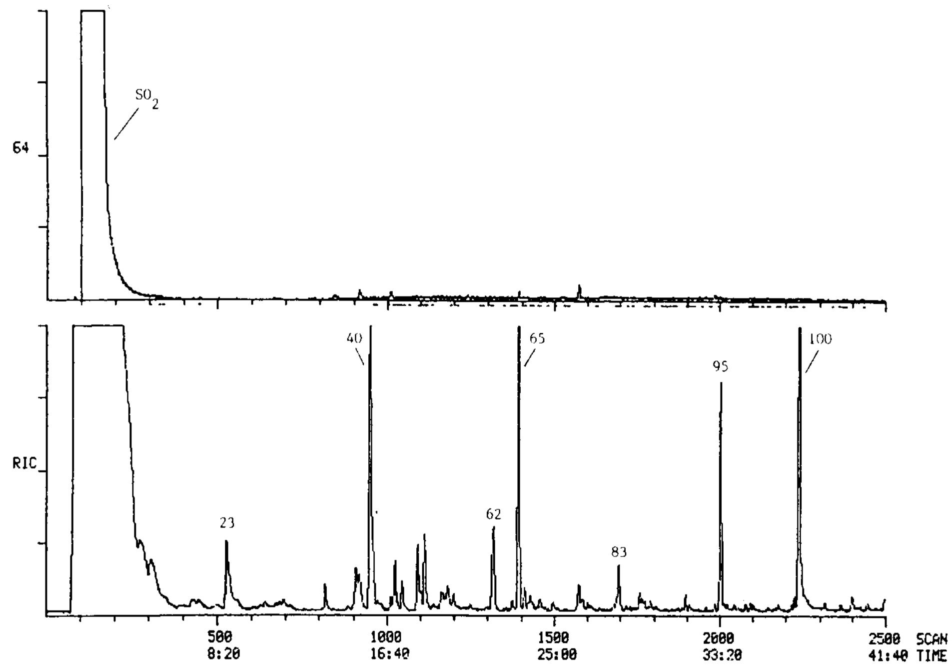


Fig. 2. Pyrolysis–gas chromatogram and mass fragmentogram of m/z 64 (SO_2, M^+) of a caramel colour, class II; capillary column (b).

data system of the mass spectrometer, this method was simulated by data enhancement and addition of all spectra generated by pyrolysis–GC/MS of a caramel colour (mass range m/z 48–190). Fig. 3 shows the simulated pyrolysis–mass spectra of the four classes of caramels.

The range of qualitative and quantitative differences apparent in Fig. 3 suggest that the classification of an unknown caramel colour is practicable although caramels of class II cannot be easily distinguished from those of class IV. Class II caramels are of no relevance in the Federal Republic of Germany. Such composite pyrolysis–mass spectra enable the quantitative comparison of an unknown with reference spectra stored in a mass spectra library (purity, fit values) by the library search algorithm [5].

The procedure described combines the advantages of pyrolysis–MS, such as rapid and easy interpretability of the results and the applicability of statistical methods, with those of pyrolysis–GC/MS. Only the latter technique produces unambiguous information about the nature and amount of the pyrolysis products formed.

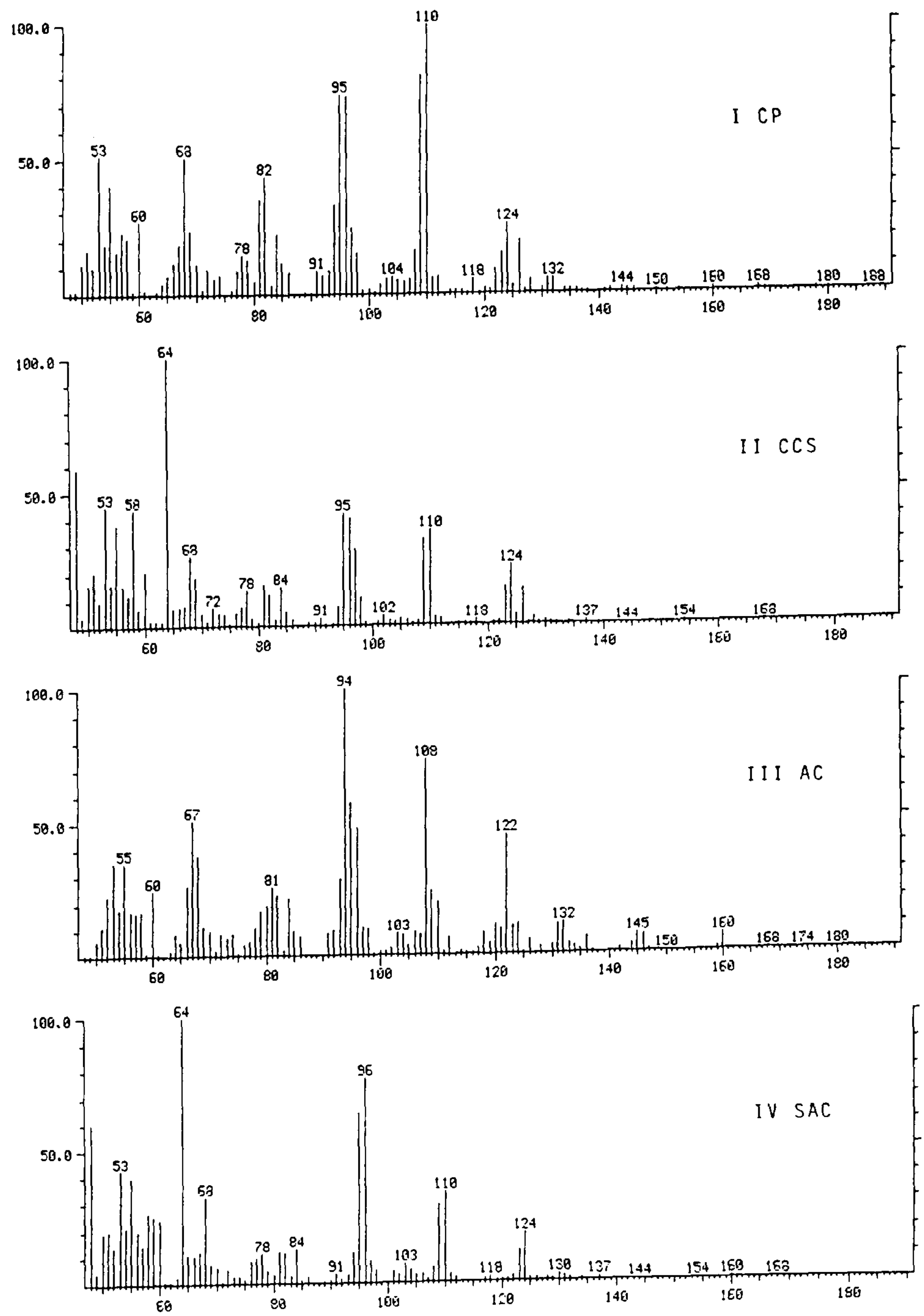


Fig. 3. Simulated pyrolysis–mass spectra of caramel colours.

REFERENCES

1 International Technical Caramel Association, Caramel Colors — Classification and Specification System, Washington, DC, 1979.
2 R. Hardt and W. Baltes, J. Anal. Appl. Pyrolysis, 13 (1988) 191.
3 R. Hardt and W. Baltes, Z. Lebensm. Unters. Forsch., 185 (1987) 275.
4 A. Dross, R. Hardt and W. Baltes, Fresenius Z. Anal. Chem., 328 (1987) 495.
5 N.L. Bakowski, E.C. Bender and T.O. Munson, J. Anal. Appl. Pyrolysis, 8 (1985) 483.