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Simultaneous determination of sorbic acid, dehydroacetic acid and benzoic acid by gas chromatography–mass spectrometry

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ABSTRACT

A method for the simultaneous determination of sorbic acid, dehydroacetic acid and benzoic acid using gas chromatography–chemical ionization mass spectrometry is described. The three components were separated on diethylene glycol succinate and eluted in the order of sorbic acid, dehydroacetic acid and then benzoic acid. In chemical ionization, the multiple-ion monitor is set to the quasi-molecular ion, that is m/z 113 for sorbic acid, m/z 169 for dehydroacetic acid and m/z 123 for benzoic acid. The linear dynamic detection range was approximately $1 \cdot 10^3$ ($5 \cdot 10^{-10}$ to $5 \cdot 10^{-7}$ g). The minimum detectable amounts of the three components were found to be 200–500 pg. The chemical ionization mass fragmentographic method was about ten-fold more sensitive than the electron impact method. This method was sensitive and selective without any influence of solvent peak and other contaminants. The method has been applied to the determination of preservatives in foods.

INTRODUCTION

Recently many kinds of preservatives have been used to protect food, pharmaceutical and cosmetic products from damage by oxidation as well as microbial and fungal attack. Sorbic acid, dehydroacetic acid and benzoic acid are used extensively as preservatives in foods. They are added to food individually or as mixtures, and hence simultaneous determination is required.

In general, extraction or clean-up of three components from a sample is accomplished by homogenization followed by steam distillation [1,2] or liquid–liquid partition [3,4]. In other cases, *e.g.*, liquid samples such as soft drinks, only dilution with solvent is necessary [5,6].

The determination of three components individually or collectively has been reported using titration [7,8], visible or UV spectrometry [4,9,10], high-performance liquid chromatography (HPLC) [1,11–13] and gas chromatography (GC) [2,14–16]. In the case

of GC, they are determined after derivatization of the acid. In any case, detection is accomplished by flame ionization detection (FID).

The author regards multiple-ion monitoring in GC–mass spectrometry (MS) as a sensitive and selective detection method in comparison with FID. This is because multiple-ion monitoring is not susceptible to interference by contaminants in the sample.

In this paper, the simultaneous determination of sorbic, dehydroacetic and benzoic acids by GC–MS utilizing chemical ionization is reported.

EXPERIMENTAL

Chemicals and reagents

Sorbic acid, dehydroacetic acid and benzoic acid were guaranteed reagents from Tokyo Kasei Kogyo (Tokyo, Japan). Diethyl ether, acetone and other solvents and chemicals were of analytical-reagent grade and obtained from Wako (Tokyo, Japan).

Instrumentation

GC–MS was performed on a NEVA GC–MS TE 600 S System (Nichiden Varian, Japan). The GC column used was 200 cm × 2 mm I.D. Pyrex glass tubing packed with 5% diethylene glycol succinate (DEGS) on Neosorb NS (pretreated with phosphoric acid, 80–100 mesh). The column temperature was 160 or 170°C and the carrier gas flow-rate was 10 m/min. MS conditions were as follows: total ion current (TIC), 180 μA; electron accelerated voltage, 70 V; ion accelerated voltage, 10.6 V; secondary electron multiplier voltage, -2.5 kV; reagent gas, methane.

Sample

The samples were commercially available foodstuffs consisting of cheese, jam, marmalade, juice and cuttlefish.

Procedures

The samples (2 g) were weighed, and 2 ml of saturated sodium chloride solution and 2 ml of 10% sulphuric acid were added to the samples, which were then homogenized. The homogenized samples were extracted twice with 20 and 10 ml of diethyl ether. The extracts were combined and washed with 4 ml of saturated sodium chloride solution and then dried with anhydrous sodium sulphate and evaporated. The residue was dissolved in 1 ml of acetone, and 2 μl of this solution were injected into the GC–MS system.

RESULTS AND DISCUSSION

Gas chromatographic separation

Sorbic, dehydroacetic and sorbic acids were well separated using DEGS on Neosorb NS (80–100 mesh pretreated phosphoric acid) in a glass column. Under these conditions, tailing of the chromatographic peaks was absent. Typical TIC chromatograms are shown in Fig. 1. Sorbic, dehydroacetic and benzoic acids are eluted within 4 min.

Mass spectra

The electron impact (EI) and chemical ionization (CI) mass spectra of sorbic, dehydroacetic and benzoic acids are shown in Figs. 2, 3 and 4, respectively.

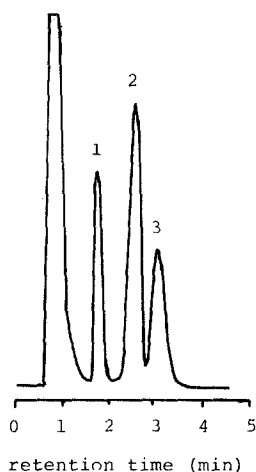The EI mass spectrum of sorbic acid in Fig. 2 is

Fig. 1. Typical chromatogram of sorbic acid (1), dehydroacetic acid (2) and benzoic acid (3) on DEGS at 160°C.

characterized by molecular ion peaks at m/z 112 and m/z 97, corresponding to elimination of CH_3, (M − 15) and at m/z 67 caused by elimination of COOH (M − 45). The CI (CH_4) mass spectrum of sorbic acid (Fig. 2, bottom) is characterized by a quasi-molecular peak, M + 1 (m/z 113), and weak fragment peaks for M + 29 (m/z 141) and M + 41 (m/z 153) arising from $C_2H_5^+$ and $C_3H_5^+$ ions as a result of methane ionization. Additionally, the m/z 97 peak appeared to be due to (M − 15 + 1).

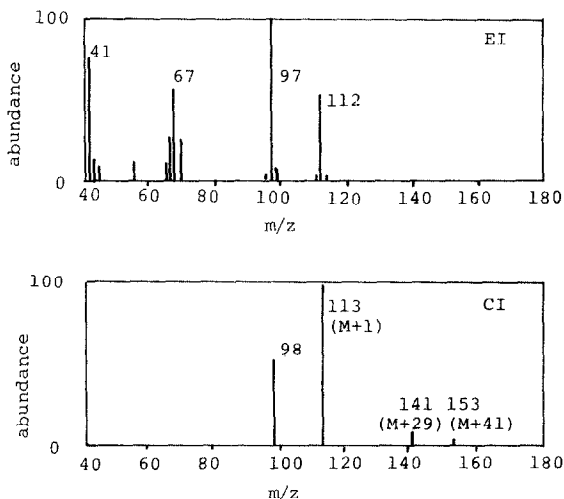The EI mass spectrum of dehydroacetic acid in Fig. 3 shows a peak at m/z 168, a molecular peak of

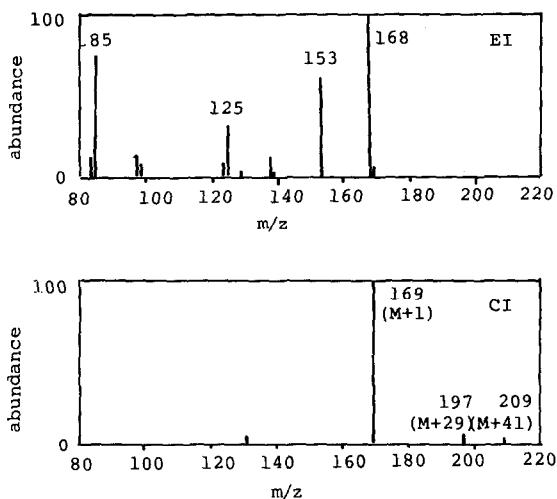Fig. 2. EI and CI mass spectra of sorbic acid.

Fig. 3. EI and CI mass spectra of dehydroacetic acid.

medium intensity at m/z 153 due to loss of CH_3 (M − 15) and a peak at m/z 125 caused by loss of CO (M − 43). The CI mass spectrum of dehydroacetic acid (Fig. 3, bottom) consists of peaks at m/z 169 (M + 1), m/z 197 (M + 29) and m/z 209 (M + 41).

The EI mass spectrum of benzoic acid (Fig. 4) consists of the molecular ion peak at m/z 122; other prominent peaks are those at m/z 105 caused by loss of OH (M − 17) and at m/z 77 due to loss of COOH (M − 45). The CI mass spectrum reveals quasi-molecular ion peaks at m/z 123 (M + 1) and m/z 106 (105 + 1). The principal advantages of CI over EI
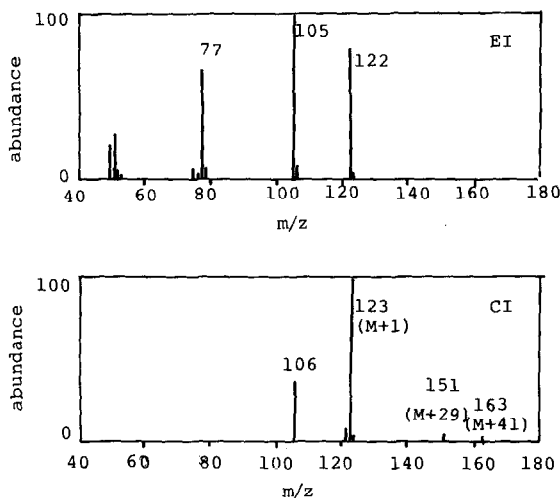

Fig. 4. EI and CI mass spectra of benzoic acid.

are simple fragmentation patterns and strong peaks related to the molecular ion.

Mass fragmentography

CI mass fragmentography is appropriate for the simultaneous determination of a small number of different structural components. Accordingly, the multiple-ion monitor was set to the quasi-molecular ion (M + 1) of each compound, that is m/z 113 for sorbic acid, m/z 169 for dehydroacetic acid and m/z 123 for benzoic acid. Fig. 5 shows the fragmento-
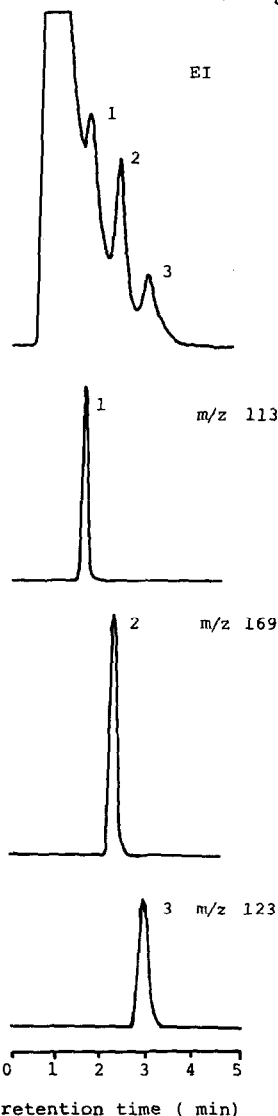

Fig. 5. CI mass fragmentograms of sorbic acid (1), dehydroacetic acid (2) and benzoic acid (3), 30 ng each, on DEGS at 170°C.

TABLE I

RECOVERIES OF SORBIC ACID, DEHYDROACETIC ACID AND BENZOIC ACID FROM FOODS

Compound	Average (%)	R.S.D. ($n = 3$) (%)
Strawberry jam		
Sorbic acid	98 ± 3	2.2
Dehydroacetic acid	101 ± 2	1.8
Benzoic acid	102 ± 2	1.9
Cheese		
Sorbic acid	97 ± 5	3.7
Dehydroacetic acid	99 ± 4	3.0
Benzoic acid	95 ± 6	4.5

gram of settings m/z 113, 169 and 123. The large solvent peak interfered with the sorbic, dehydroacetic and benzoic acids peaks in the TIC 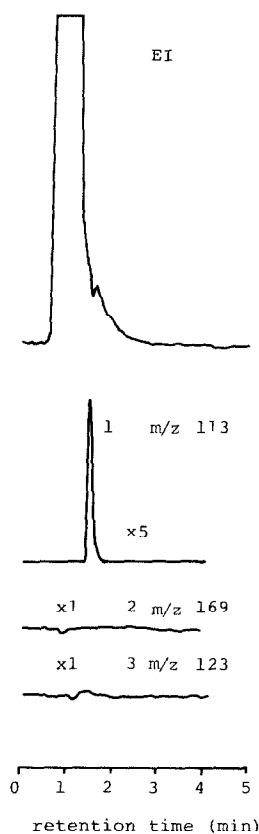chromatogram, whereas in the CI mass fragmentogram every peak was detected sensitively and selectively without any interference.

Linearity and minimum detectable amounts

A linear correlation was observed between $5 \cdot 10^{-10}$ and $5 \cdot 10^{-7}$ g. The minimum detectable amounts were determined until a signal-to-noise ratio of 3 was reached. In this way, the minimum detectable amounts obtained were 200 pg for dehydroacetic acid, 300 pg for sorbic acid and 500 pg for benzoic acid. The sensitivity of the CI mass fragmentography method was about ten-fold greater than that of the EI method.
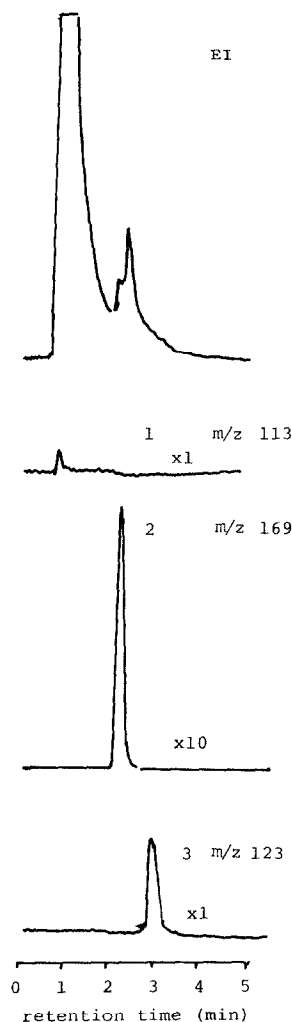

Fig. 6. Chromatograms of commercial orange marmalade.

Fig. 7. Chromatograms of commercial cheese.

TABLE II

DETERMINATION OF SORBIC ACID, DEHYDRO-ACETIC ACID AND BENZOIC ACID IN FOODS

	Contents (ppm)		
	Sorbic acid	Dehydroacetic acid	Benzoic acid
Strawberry jam	200	–	–
Orange marmalade	224	–	–
Smoked cuttlefish	560	–	–
Concentrated orange juice	–	–	570
Cheese	–	280	10
Cheese (slice)	1000	–	8

Determination of sorbic, dehydroacetic and benzoic acids in foods

Recoveries were determined by adding 100 ppm sorbic, dehydroacetic and benzoic acids to blank homogenized strawberry jam and cheese from which it had been previously confirmed that the three components were absent. The results are given in Table I. The recoveries ranged from 95 to 102% with a relative standard deviation (R.S.D.) of 1.7–4.5%.

This method was applied to the determination of sorbic, dehydroacetic and benzoic acids in jam, juice and cheese, etc. The results are shown in Table II. Typical chromatograms of orange marmalade and cheese are shown in Figs. 6 and 7, respectively. The preservatives contained in each food were described on the labels, but not the types or quantities.

Using this method, sorbic acid, dehydroacetic acid and benzoic acid were simultaneously determined using the multiple-ion monitor set to the quasi-molecular peak of m/z 113, 169 and 123 in the CI mass fragmentograph. This method was selective without interference from other contaminants or the solvent peak. The sensitivity of the method was such that 200–500 pg amounts of each component could be detected.

REFERENCES

1 H. Terada and Y. Sakabe, *J. Chromatogr.*, 346 (1985) 333.
2 I. Saito, H. Oshima, N. Kawamura, K. Uno and M. Yamada, *J. Assoc. Off. Anal. Chem.*, 70 (1987) 507.
3 F. Ureta, *Connaiss. Vigne Vin.*, 18 (1984) 287.
4 O. W. Law, S. F. Luk and R. K. M. Lam, *Analyst (London)*, 114 (1989) 217.
5 T. Mine and M. Horiuchi, *Shokuhin Eiseigaku Zasshi*, 26 (1985) 61.
6 J. T. Hann and S. I. Gilkison, *J. Chromatogr.*, 395 (1987) 317.
7 F. X. Demers and R. L. Yates, *J. Assoc. Off. Anal. Chem.*, 65 (1982) 82.
8 O. W. Law and S. F. Luk, *Analyst (London)*, 112 (1987) 1269.
9 J. Dumain, A. Parmentier, C. Banner and F. M. Pailler, *Ann. Falsif. Expert. Chim. Toxicol.*, 80 (1987) 85.
10 G. Schwedt and K. Schwardorf, *Inst. Lebensmittelchem.*, 82 (1986) 209.
11 H. S. Lee, R. L. Rouseff and J. F. Fisher, *J. Food Sci.*, 51 (1986) 568.
12 K. Fujimura and M. Tsuchiya, *Bunseki Kagaku*, 37 (1988) 56.
13 F. J. E. M. Kueppers and J. A. Jans, *J. Assoc. Off. Anal. Chem.*, 71 (1988) 1068.
14 Y. Chen, Q. Li, L. He and L. Zheng, *Sepu*, 5 (1987) 238.
15 D. H. Daniels, C. R. Warner, S. Selim and F. L. Joe, *J. Assoc. Off. Anal. Chem.*, 66 (1983) 893.
16 I. M. Perl, M. P. Szakacs and M. Morvai, *Magy. Kem. Foly.*, 93 (1987) 71.