Journal of Chromatography, 547 (1991) 291–298
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 216

Determination of volatile aliphatic aldehydes in the headspace of heated food oils by derivatization with 2-aminoethanethiol

AKIO YASUHARA*
Regional Environment Division, National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, Ibaraki 305 (Japan)
and
TAKAYUKI SHIBAMOTO
Department of Environmental Toxicology, University of California, Davis, CA 95616 (USA)
(Received December 10th, 1990)

ABSTRACT

Reaction conditions for the derivatization of volatile aliphatic aldehydes with 2-aminoethanethiol (cysteamine) were investigated. Reaction at room temperature for 1 h at pH 8 was sufficient and the recovery was quantitative for all the aldehydes tested. The detection limits were very low with a nitrogen–phosphorus detector. Concentration of the extract solution cannot be used because of the high volatility of the derivatization products, thiazolidines. Eleven aldehydes in the headspace of heated food oils were determined by this derivatization method. The concentration of hexanal was very high in all samples. It is noteworthy that the contents of isoalkanals were very low.

INTRODUCTION

The formation of many carbonyl compounds, particularly volatile aldehydes, by oxidation or decomposition of foodstuffs which contain lipids has already been reported [1–5]. As volatile aliphatic aldehydes have offensive smells, great attention has been paid to analytical methods for these aldehydes with regard to the odour control of exhaust gases from the paint and printing industries which include heating processess [6].

Many analytical methods for volatile aldehydes have been developed. Derivatization with 2,4-dinitrophenylhydrazine [7–9], benzyloxyamine [10], pentafluorobenzyloxyamine [11,12], or N-benzylethanolamine [13,14] are well known. However, peak identification is extremely difficult because the formation of both *syn* and *anti* forms is inevitable. Therefore, it is almost impossible to determine different aldehydes simultaneously by these derivatization methods. Derivatization with 2-hydroxy methylpiperidine has been recommended in the OSHA method for the determination of both formaldehyde and acrolein [15]. However, this method is not applicable to the determination of other aldehydes because excess of the reagent, 2-hydroxymethyl-

0021-9673/91/$03.50

piperidine, interferes. Recently, Shibamoto and co-workers [16–18] developed a new derivatization method with 2-aminoethanethiol (cysteamine). This method has several characteristics compared with other derivatization methods: (1) only one derivative is formed from one aldehyde; (2) the derivatization reaction proceeds under very mild conditions, rapidly and with almost quantitative yield; (3) the derivatives, thiazolidines, can be separated perfectly with fused-silica capillary column and detected selectively with a nitrogen–phosphorus detector; and (4) excess of the reagent, 2-aminoethanethiol, does not interfere with gas chromatographic (GC) analysis.

We have already reported results for aldehydes and ketones in the headspace of heated pork fat, obtained using the derivatization method with cysteamine [19]. However, details of this analytical method have not been reported previously. This paper describes the reliability of this method and its application to the headspace analysis of heated food oils.

EXPERIMENTAL

Reagents

Cysteamine hydrochloride was purchased from Aldrich and aldehydes from Wako. Pure thiazolidines as derivatization products were synthesized according to the literature.

Sampling and analytical procedure

Cysteamine hydrochloride (0.5 g) was dissolved in 15 ml of distilled water and the pH was adjusted to 8.0 with 0.1 *M* sodium hydroxide solution. The final volume of the solution was set at 20 ml. This solution was sucked through a sample gas inlet into a sampling bottle, which was evacuated by a vacuum pump before sampling. The volume of the sampling bottle was 1020 ml. The set-up is shown in Fig. 1.

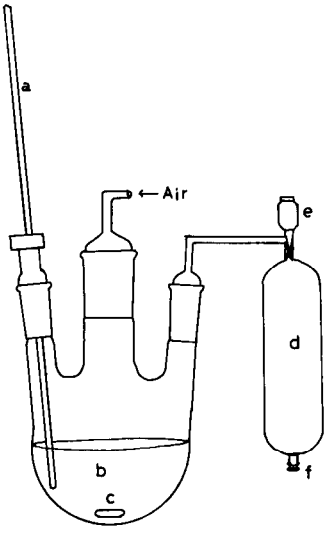

Fig. 1. Apparatus for sampling headspace of heated food oil. a = Thermometer; b = food oil; c = bar for magnetic stirrer; d = sampling bottle; e = needle valve; f = glass stopper.

Food oils used as samples were corn oil, corn oil used for a long period, cottonseed oil, a mixture of soybean oil and sesame oil and safflower oil. All these oils are widely used in most Japanese homes for cooking. A 100-g amount of each oil was placed in a 2-l three-necked round flask and heated at 200°C with magnetic stirring. The sampling bottle containing cysteamine solution prepared as described above was connected to the flask as shown in Fig. 1. Headspace was sucked into the bottle by loosening a needle valve. After sampling, the bottle was shaken vigorously for 5 min and then kept for 1 h at room temperature for completion of derivatization. Next, the solution was transferred to a separating funnel and extracted twice with dichloromethane (10 and 5 ml). The combined organic layer was passed through a small amount of anhydrous sodium sulphate for removal of water and the sodium sulphate was washed with dichloromethane (5 ml). Both dichloromethane solutions were combined. A 20-μl volume internal standard (N-methylacetamide) solution (12.2 mg/ml in dichloromethane) was added to the solution and the final volume was adjusted to 20 ml.

Gas chromatography

A Hewlett-Packard Model 5890A gas chromatograph equipped with a DB-WAX (0.25 μm) fused-silica capillary column (30 m × 0.25 mm I.D.) and a nitrogen–phosphorus detector was used. The column oven temperature was held at 40°C for 2 min and then programmed to 180°C at 4°C/min. The GC peak areas were integrated with a System Instruments Model 7000B integrator. The injector temperature was 250°C and the detector temperature 300°C. The carrier gas (helium) flow-rate was 33.7 cm/s. The injector splitting ratio was 1:20.

Gas chromatography–mass spectrometry

The GC conditions were similar to those described above. A JEOL Model DX-300 mass spectrometer equipped with a Hewlett-Packard Model 5710A gas chromatograph and a JEOL Model JMA-3500 data acquisition and analysis system was used for measurements of mass spectra. The mass spectrometric conditions were as follows: ion-source pressure, $3 \cdot 10^{-6}$ Torr; ion-source temperature, 190°C; ionization energy, 70 eV; ionization current, 300 μA; accelerating voltage, 3 kV; scan range, m/z 10–400; scan speed, 1.4 per scan; repetition time, 2 s; coupling mode for gas chromatograph and mass spectrometer, direct.

RESULTS AND DISCUSSION

Effect of pH on derivatization

Recovery was measured by reacting 100 μg of each aldehyde with 0.5 g of cysteamine for 3 h at various pH values and the results are shown in Table I, with blank values substracted for formaldehyde and acetaldehyde. The reaction seems to proceed completely at pH $\geqslant$ 8. As alkaline conditions are not favourable for sample preparation, pH 8 was adopted.

Effect of reaction time on derivatization

Recovery was investigated by reacting 100 μg of each aldehyde with 0.5 g of cysteamine at pH 8 for various reaction times and the results are shown in Table II,

TABLE I

RECOVERY ON DERIVATIZATION WITH CYSTEAMINE AT VARIOUS pH VALUES

Blank values were subtracted for formaldehyde and acetaldehyde.

pH	Recovery (%)										
	C_1	C_2	C_3	i-C_4	C_4	i-C_5	C_5	C_6	C_7	C_8	C_9
6	37	54	93	96	94	96	96	72	85	89	81
7	95	90	99	98	98	98	97	81	87	98	88
8	94	103	104	101	103	99	102	95	91	99	94
9	100	103	101	100	102	99	101	95	87	99	99
10	99	104	102	101	103	101	104	99	95	99	97
11	99	103	101	102	104	99	103	98	97	99	98

with blank values subtracted for formaldehyde and acetaldehyde. The necessary reaction time is 1 h, as the reaction rate is fast.

Blank test

Blank values were observed only for formaldehyde and acetaldehyde, probably present in the solvent and distilled water. The values were 7.21 μg for formaldehyde and 9.63 μg for acetaldehyde when 15 ml of dichloromethane and 20 ml of distilled water were used for extraction and dissolution of cysteamine hydrochloride, respectively.

Reliability of analytical procedure

Replicate recoveries were measured by reacting 0.5 g of cysteamine and 100 μg of each aldehyde at pH 7 for 3 h and the results are given in Table III with blank values substracted for formaldehyde and acetaldehyde. The high standard deviations for formaldehyde and acetaldehyde seem to be due to the deviation of the blank values.

Detection limit

Detection limits, shown in Table IV, were calculated from the peak height with a signal-to-noise ratio of 3 using split-mode injection. The detection limits were

TABLE II

EFFECT OF REACTION TIME ON DERIVATIZATION

Blank values were subtracted for formaldehyde and acetaldehyde

Time (h)	Recovery (%)										
	C_1	C_2	C_3	i-C_4	C_4	i-C_5	C_5	C_6	C_7	C_8	C_9
1	91	99	93	89	89	90	88	83	88	99	93
2	92	101	95	92	91	93	90	88	89	100	94
3	94	92	97	96	94	98	93	90	91	101	95
4	94	92	96	95	95	97	92	91	90	99	96

TABLE III

REPRODUCIBILITY OF RECOVERY ON DERIVATIZATION

Blank values were subtracted for formaldehyde and acetaldehyde.

Run No.	Recovery (%)										
	C_1	C_2	C_3	i-C_4	C_4	i-C_5	C_5	C_6	C_7	C_8	C_9
1	108	109	98	95	94	96	97	98	97	96	91
2	88	92	97	95	93	95	95	97	94	95	88
3	93	95	98	95	94	95	95	98	98	91	90
4	99	98	100	97	97	99	99	104	99	100	99
5	90	90	98	95	97	98	97	101	95	99	90
Av.	96	97	98	95	95	97	97	100	97	96	92
R.S.D. (%)[a]	8	8	1	1	2	2	2	3	2	4	5

[a] Relative standard deviation.

roughly proportional to molecular weight, as the relative nitrogen content in the molecules decreases with increasing molecular weight.

Loss of thiazolidines by concentrating dichloromethane solution

A 10-μg amount of each thiazolidine was dissolved in 80 ml of dichloromethane and the solution was concentrated to 2 ml by distillation under atmospheric pressure. Losses of thiazolidines in this procedure are shown in Table V. These results suggest that concentration by distillation should not be adopted.

Application to headspace of heated food oil

Typical gas chromatograms are shown in Figs. 2 and 3. Table VI gives the analytical results. The contents of isoalkanals such as isobutyraldehyde and isovaleraldehyde were low compared with the *n*-alkanals. The abundance of hexanal was the highest in every instance. These trends were the same as the results for the headspace

TABLE IV

DETECTION LIMITS OF THIAZOLIDINES AND CORRESPONDING ALDEHYDES

Substance	Detection limit (pg)	Corresponding aldehyde (pg)
Thiazolidine	17.2	5.8
2-Methylthiazolidine	16.7	7.1
2-Ethylthiazolidine	20.2	10.0
2-Isopropylthiazolidine	22.7	12.5
2-Propylthiazolidine	26.1	14.4
2-Isobutylthiazolidine	30.4	18.0
2-Butylthiazolidine	32.8	19.5
2-Pentylthiazolidine	39.2	24.7
2-Hexylthiazolidine	42.8	28.2
2-Heptylthiazolidine	53.3	36.5
2-Octylthiazolidine	51.3	36.2

TABLE V

LOSS OF THIAZOLIDINES DURING CONCENTRATION PROCESS

Substance	Loss (%)	Substance	Loss (%)
Thiazolidine	59	2-Butylthiazolidine	37
2-Methylthiazolidine	46	2-Pentylthiazolidine	31
2-Ethylthiazolidine	42	2-Hexylthiazolidine	19
2-Isopropylthiazolidine	35	2-Heptylthiazolidine	8
2-Propylthiazolidine	39	2-Octylthiazolidine	3
2-Isobutylthiazolidine	34		

of heated pork fat [19]. These results suggest that the oxidative cleavage of the double bond in natural unsaturated fatty acid esters such as linoleic acid esters produces hexanal [2]. It is noteworthy that large amounts of these saturated aliphatic aldehydes (C_1-C_9) were formed by heating food oils. It has been confirmed by mass spectrometry that mass spectra at peaks corresponding to thiazolidines in GC were coincident with the reported values [20,21]. As a strong common peak exists at *m/z* 88 in the mass spectra of 2-alkylthiazolidines, mass chromatography at *m/z* 88 is very effective for the detection of thiazolidines derived from aldehydes. Fig. 4 shows a typical example. Mass chromatography at *m/z* 102 is performed for detection of 2-alkanones,

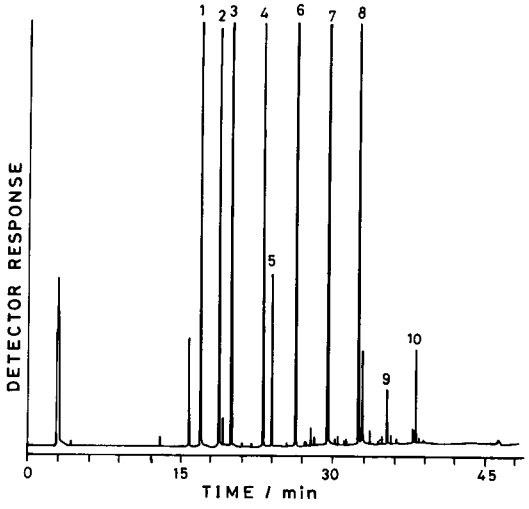

Fig. 2. Gas chromatogram of derivatives from aldehydes in headspace of heated safflower oil. Peaks: 1 = 2-methylthiazolidine from acetaldehyde; 2 = thiazolidine from formaldehyde; 3 = 2-ethylthiazolidine from propionaldehyde; 4 = 2-propylthiazolidine from butyraldehyde; 5 = internal standard (N-methylacetamide); 6 = 2-butylthiazolidine from valeraldehyde; 7 = 2-pentylthiazolidine from hexanal; 8 = 2-hexylthiazolidine from heptylaldehyde; 9 = 2-heptylthiazolidine from octylaldehyde; 10 = 2-octylthiazolidine from nonylaldehyde.

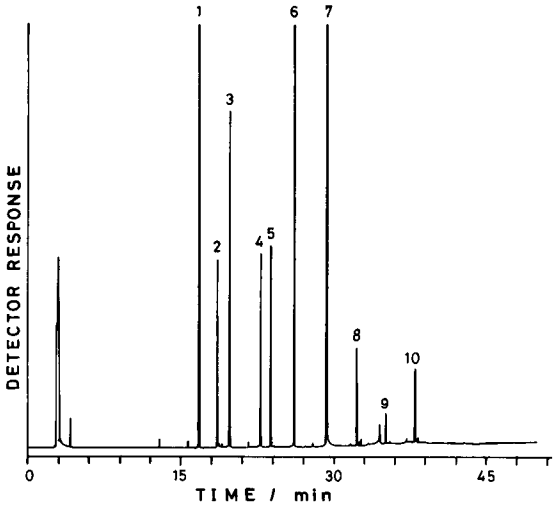

Fig. 3. Gas chromatogram of derivatives from aldehydes in headspace of heated corn oil. Peaks: 1 = 2-methylthiazolidine from acetaldehyde; 2 = thiazolidine from formaldehyde; 3 = 2-ethylthiazolidine from propionaldehyde; 4 = 2-propylthiazolidine from butyraldehyde; 5 = internal standard (N-methylacetamide); 6 = 2-butylthiazolidine from valeraldehyde; 7 = 2-pentylthiazolidine from hexanal; 8 = 2-hexylthiazolidine from heptylaldehyde; 9 = 2-heptylthiazolidine from octylaldehyde; 10 = 2-octylthiazolidine from nonylaldehyde.

TABLE VI

CONCENTRATIONS OF ALDEHYDES IN HEADSPACE OF HEATED FOOD OILS

Unit of concentration is μg/l of headspace on 100 g of heated food oil. Concentration values are averages of three replicate measurements.

Aldehyde	Food oil				
	Fresh corn	Used corn	Cotton-seed	Safflower	Mixed oil[a]
C_1	53	72	99	85	46
C_2	583	859	576	1130	572
C_3	286	745	232	797	475
i-C_4	2	4	ND	3	ND
C_4	174	317	161	622	140
i-C_5	3	4	ND	ND	ND
C_5	714	548	630	1550	413
C_6	2570	1480	2220	4700	1390
C_7	179	326	180	1230	165
C_8	77	147	77	143	72
C_9	162	513	181	251	263

[a] Mixture of soybean oil and sesame oil.

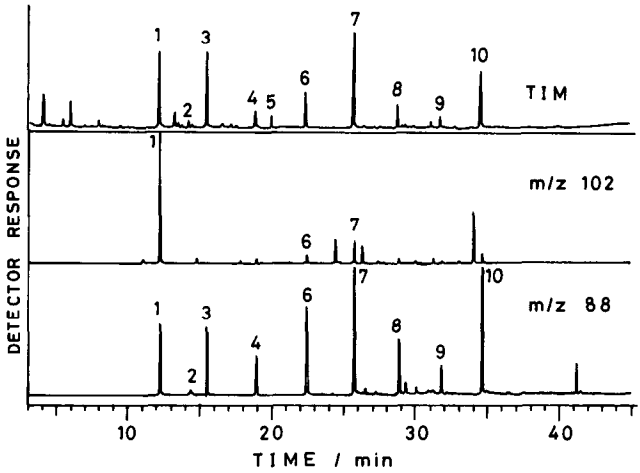

Fig. 4. Mass chromatogram of derivatives from aldehydes in headspace of heated mixture of soybean oil and sesame seed oil. TIM = total ion monitoring. Peaks: 1 = 2-methylthiazolidine from acetaldehyde; 2 = thiazolidine from formaldehyde; 3 = 2-ethylthiazolidine from propionaldehyde; 4 = 2-propylthiazolidine from butyraldehyde; 5 = internal standard (N-methylacetamide); 6 = 2-butylthiazolidine from valeraldehyde; 7 = 2-pentylthiazolidine from hexanal; 8 = 2-hexylthiazolidine from heptylaldehyde; 9 = 2-heptylthiazolidine from octylaldehyde; 10 = 2-octylthiazolidine from nonylaldehyde.

because thiazolidines derived from 2-alkanones show a strong common peak at *m/z* 102 in their mass spectra.

It is concluded that the described method is very effective for the determination of aldehydes.

REFERENCES

1 T. Yamamoto, T. Kurata, H. Kato and M. Fujimaki, *Agric. Biol. Chem.*, 34 (1970) 88.
2 D. S. Mottram, R. A. Edwards and H. J. H. MacFie, *J. Sci. Food Agric.*, 33 (1982) 934.
3 B. Reindl and H. J. Stan, *J. Agric. Food Chem.*, 30 (1982) 849.
4 D. S. Mottram, S. E. Croft and R. L. S. Patterson, *J. Sci. Food Agric.*, 35 (1984) 233.
5 S. Ohnishi and T. Shibamoto, *J. Agric. Food Chem.*, 32 (1984) 987.
6 Japan Environment Agency, *Personal communication.*
7 D. Grosjean, *Environ. Sci. Technol.*, 16 (1982) 254.
8 K. Kuwata, M. Uebori, H. Yamasaki and Y. Kuge, *Anal. Chem.*, 55 (1983) 2013.
9 S. B. Tejada, *Int. J. Environ. Anal. Chem.*, 26 (1986) 167.
10 S. P. Levine, T. M. Harvey, T. J. Waeghe and R. H. Shapiro, *Anal. Chem.*, 53 (1981) 805.
11 H. Nishikawa, Y. Takahara, H. Mori and T. Hayakawa, *J. Jpn. Soc. Air Pollut.*, 19 (1984) 387.
12 H. Nishikawa, T. Hayakawa and T. Sakai, *Bunseki Kagaku*, 36 (1987) 381.
13 E. R. Kennedy and R. H. Hill, Jr., *Anal. Chem.*, 54 (1982) 1739.
14 *NIOSH Manual of Analytical Methods*, US National Institute for Occupational Safety and Health, 1984, Method 2502.
15 *OSHA Manual of Analytical Methods*, US Department of Labor–Occupational Safety and Health Administration, 1985, Method 52.
16 T. Hayashi and T. Shibamoto, *J. Agric. Food Chem.*, 33 (1985) 1000.
17 T. Hayashi, C. A. Reece and T. Shibamoto, *J. Assoc. Off. Anal. Chem.*, 69 (1986) 101.
18 K. Umano and T. Shibamoto, *J. Agric. Food Chem.*, 35 (1987) 14.
19 A. Yasuhara and T. Shibamoto, *J. Food Sci.* 54 (1984) 1471.
20 A. Yasuhara and T. Shibamoto, *Agric. Biol. Chem.*, 53 (1989) 2273.
21 A. Yasuhara, H. Ito, T. Mizoguchi, T. Uehiro, J. Shindo, R. Shinohara, Y. Shirane, K. Kenmotsu, T. Okumura and K. Imamura, *NIES Mass Spectral Data Base for Environmental Analysis*, Techno Culture Tsukuba, Tsukuba, 2nd ed., 1990, p. 1148.