

Analysis of Aldehydes in Water by Head Space-GC/MS

Naeko Sugaya,^{*,a} Tomoo Nakagawa,^a Katsumi Sakurai,^a Masatoshi Morita,^b and Sukeo Onodera^c

^aYokohama City Institute of Health, 1–2–17 Takigashira, Isogo-ku, Yokohama 235–0012, Japan, ^bNational Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, Ibaraki 305–0061, Japan, and ^cFaculty of Pharmaceutical Sciences, Tokyo University of Science, 12 Ichigawa-funagawara-machi, Shinjuku-ku, Tokyo 162–0826, Japan

(Received July 3, 2000; Accepted September 26, 2000)

The concentrations of formaldehyde, acetaldehyde, propionaldehyde, and *n*-butyraldehyde in water were quantitatively determined by head space-gas chromatography/mass spectrometry (HS-GC/MS). Aqueous aldehydes were treated with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) in a sealed vial at 60°C for 60 min. Head space was then analyzed by GC/MS. In comparison with electron ionization (EI) mass spectra, negative chemical ionization (NCI) mass spectra of PFBOA derivatives gave more spectral peaks of structural origin and with simple, characteristic fragmentation patterns. HS-GC/MS is highly sensitive for aqueous aldehydes because it eliminates interference from the water sample. The concentrations of various aldehydes in tap water and commercial mineral water were determined by HS-GC/MS. The following concentration ranges were detected for the individual aldehydes; formaldehyde, not detected (N.D.)–59 µg/l; acetaldehyde, N.D.–260 µg/l; propionaldehyde, N.D.–0.9 µg/l; and *n*-butyraldehyde, N.D.–0.3 µg/l.

Key words — formaldehyde, *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine, head space-GC/MS, negative chemical ionization, aldehydes, water

INTRODUCTION

Aldehydes are formed by incomplete combustion of organic materials and by the photochemical reaction of hydrocarbons in the atmosphere. Aldehydes readily dissolve in ground water, and human beings may then be exposed to the contaminated water. In addition, aldehyde formation has been reported during ozonization or chlorination of source water.¹⁾ In Japan, aldehyde concentrations in tap water are monitored regularly. For instance, formaldehyde is regulated at concentration less than 80 µg/l in Japan, whereas 900 µg/l is the tap water quality guidance of WHO. However, humans consume not only tap water, but also commercial mineral water and ground water. Mineral water is a popular substitute for tap water. Some aldehydes impart unsavory tastes to water, and it has been suggested that aldehyde contamination may occur during the bottling of ground water and spring water.²⁾ Among those aldehydes detected in mineral water, formal-

dehyde and acetaldehyde are of most concern since they have been reported to be mutagenic.³⁾

Electron capture detector/gas chromatography (ECD/GC), N-P detector/gas chromatography (NPD/GC), gas chromatography/mass spectrometry (GC/MS), high performance liquid chromatography (HPLC) are known to be highly sensitive and highly selective for aldehydes in water after derivatization and subsequent solvent extraction of the target aldehydes. The most common derivatizing reagents 2,4-dinitrophenylhydrazine (2,4-DNPH)^{4,5)} 2-aminoethanethiol (cysteamine)^{6,7)} and *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA)^{8–11)} form hydrazones, thiazolidines, and hydroximes, respectively, after reacting with aldehydes. However, quantitative analyses with these methods are very difficult at lower concentrations due to possible contamination during solvent extraction. In addition, once samples contain numerous interferences, isolating operations become complicated because micro cartridge chromatography must also be performed.

The aim of the present study was to develop a sensitive and selective method for the quantitation of formaldehyde, acetaldehyde, propionaldehyde,

*To whom correspondence should be addressed: Yokohama City Institute of Health, 1–2–17 Takigashira, Isogo-ku, Yokohama 235–0012, Japan. Tel.: +81-45-754-9800; FAX: +81-45-754-2210; E-mail address: gabor@yha.att.ne.jp

Table 1. Operational Conditions of GC/MS and Headspace Autosampler

GC/MS	
Column	: PTE-5 TM of Spelco(Bellfonte,USA), FUSED SILICA capillary column 30 m × 0.25 mm × 0.25 μm film thickness
Oven temperature	: 60°C (2min) → 7°C/min → 150°C → 15°/min → 220°C
Carrier gas	: He 16 psi
Injection temperature	: 200°C
Ionization voltage	: 70eV
Ion source temperature	: 200°C (EI), 150°C (NCI)
CI gas	: iso-butane (purity of 99.99%)
Headspace autosampler	
Needle temperature	: 120°C Pressurization time : 1 min
Transfer temperature	: 180°C Pressure of helium : 20 psi
Thermostic temperature	: 60°C
Thermostic time	: 60 min
Injection time	: 0.08 min

Table 2. Retention Times and SIM Monitor Ions of PFBOA Aldoximes by EI and NCI

No.	Compound	R.T.	Monitor ions (EI)	Monitor ions (NCI)
1	PFBOA formaldoxime	6.47	181, 195	181, 205, 225
2	PFBOA acetaldoxime (<i>syn</i>)	8.54	181, 209	181, 219, 239
3	PFBOA acetaldoxime (<i>anti</i>)	8.71	181, 209	181, 219, 239
4	PFBOA propionaldoxime (<i>syn</i>)	10.35	181, 236	181, 233, 253
5	PFBOA propionaldoxime (<i>anti</i>)	10.49	181, 236	181, 233, 253
6	PFBOA <i>n</i> -butyraldoxime (<i>syn</i>)	12.18	181, 239	181, 247, 267
7	PFBOA <i>n</i> -butyraldoxime (<i>anti</i>)	12.31	181, 239	181, 247, 267

R.T.: Retention time

and *n*-butyraldehyde in a water sample. Due to the high volatility of PFBOA derivatives of aldehydes, head space-gas chromatography/mass spectrometry (HS-GC/MS) was performed to determine trace amounts of aldehydes in water. The findings indicate that this method allows for rapid and accurate routine analysis that may prove useful in assessing the health implications of trace aldehydes in drinking water.

MATERIALS AND METHODS

Preparation of Reagents and Sample Solutions

- Aldehyde standard stock solutions: prepared by stepwise dilution of an aldehyde standard (Kanto Kagaku, 10000 mg/l standard mixture of formaldehyde, acetaldehyde, propionaldehyde, and *n*-butyraldehyde) with methanol.
- Internal standard solutions (50 mg/l): prepared by diluting a standard solution of 4-bromofluorobenzene (Kanto Kagaku, 1000 mg/l) with methanol.

- Blank water: Commercial mineral water (Highland Spring, Meijiya Co., Ltd.) with negligible concentrations of aldehydes
- Methanol: Kanto Kagaku (pesticide residue grade).
- PFBOA solution: PFBOA hydrochlorate (Hayashi Junyaku) was diluted with the blank water to a concentration of 1 mg/ml.
- Sodium chloride: Wako Junyaku (water quality test grade).
- Sodium thiosulfate: Wako Junyaku (reagent special grade).

Apparatus and Analytical Conditions — An HS40 head space autosampler (Perkin Elmer) was connected to a TurboMass GC/MS (Perkin Elmer). Analytical conditions are summarized in Table 1. Monitored ions and retention times of the selected ion monitoring (SIM) are summarized in Table 2.

Preparation of Standard Solutions and Sample Solutions

Standard solutions: Standard solutions were prepared by diluting 1 μl of a standard stock solution with 10 ml blank water in a head space vial. To the solutions were added 1 μl of 4-bromofluorobenzene

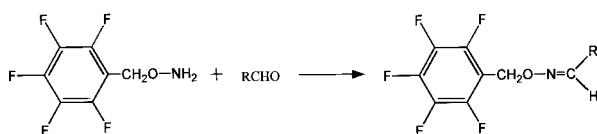


Fig. 1. Reaction of Aldehydes with PFBOA

internal standard solution, 0.6 ml of an aqueous solution of PFBOA (1 mg/ml), and 3 g sodium chloride. The vial was then immediately sealed with a polytetrafluoroethylene-lined septum and an aluminium cap. The general reaction of an aldehyde with the PFBOA derivatizing reagent is shown in Fig. 1.

Calibration curves were constructed from integrated peak areas. With the exception of formaldehyde, the total peak areas of all isomers were used.

Sample solutions: Precisely 10 ml of a water sample was measured into a head space vial, and then prepared in the same manner as the standard solutions.

Tap water was collected from Hachioji, Yokohama and Zushi cities, Japan, in November 1999. To remove residual chlorine from the tap water, an appropriate amount of sodium thiosulfate (0.02–0.05 g per 100 ml water) was added. Mineral water was purchased from local stores in Japan.

RESULTS AND DISCUSSION

Blank Water

Analyses of trace amounts of aldehydes in aqueous samples by the PFBOA derivatization method can sometimes encounter serious problems if contaminants from reagents, blank water, solvents or the laboratory environment are in high concentrations. However, HS-GC/MS allows the determination of trace amounts of aqueous aldehydes without significant contamination from organic solvents. The authors analyzed over 30 kinds of water, including mineral water, especially purified water for volatile organic compounds analysis, tap water and groundwater. Eventually, the authors selected mineral water from Meijiya Co., Ltd. as the blank water, since this water contained the lowest concentration of aldehydes.

Effects of Experimental Conditions on Reaction of Aqueous Aldehydes with PFBOA

Reaction Temperatures and Reaction Times

It is important to optimize the reaction tempera-

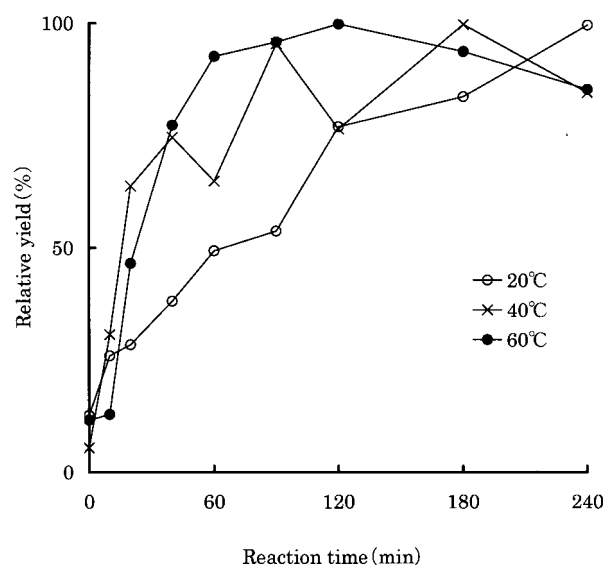


Fig. 2. Effect of Reaction Temperature and Time on PFBOA-*n*-Butyraldoxime Yield

ture and reaction time for quantitative analysis with derivatizing reagents. Many previous reports on the treatment of aqueous carbonyl compounds with PFBOA as the derivatizing reagent recommend setting the reaction temperature to room temperature or around 20°C.⁸⁾

Each aqueous aldehyde solution (10 mg/l) was prepared by adding 10 ml of blank water to a head space vial containing formaldehyde, acetaldehyde, propionaldehyde, or *n*-butyraldehyde. Subsequently, 1 ml of aqueous PFBOA solution and 3 g sodium chloride were added, and the vial was immediately sealed with a polytetrafluoroethylene-liner septum and an aluminium cap.

Optimization of reaction temperature and time was performed at 20, 40 and 60°C, and for 0–240 min. Typical PFBOA-*n*-butyraldoxime yields are shown in Fig. 2. Because all compounds reached equilibrium after about 60 min at 60°C, about 90 min at 40°C, and about 240 min at 20°C, a reaction temperature of 60°C, and a reaction time 60 min was chosen.

Salting-Out Effects

For volatile organic compounds in water, head space sampling methods are very useful, and the addition of sodium chloride useful for highly sensitive micro analysis. Addition of 3 g sodium chloride to 10 µg/l of aldehyde standard solution increased the sensitivity 2 to 3 times for all aldehydes.

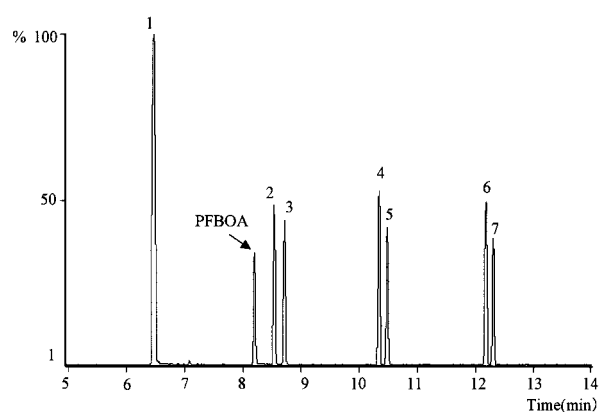


Fig. 3. NCI Chromatogram of Aldoximes

1. formaldoxime, 2. acetaldoxime (*syn*), 3. acetaldoxime (*anti*), 4. propionaldoxime (*syn*), 5. propionaldoxime (*anti*), 6. *n*-butyraldoxime (*syn*), 7. *n*-butyraldoxime (*anti*)

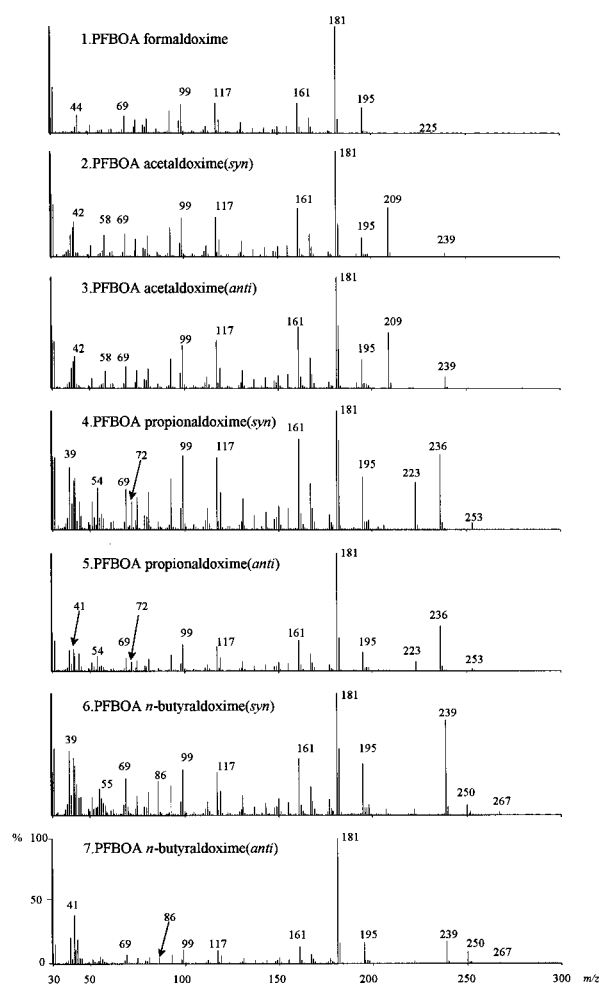


Fig. 4. Electric Ionization Mass Spectra of PFBOA Aldoxime

GC/MS Studies

Detection by Electric Ionization (EI) and Negative Chemical Ionization (NCI) for Aldehyde Measurement Using HS-GC/MS

A mass chromatogram (total ion current (TIC))

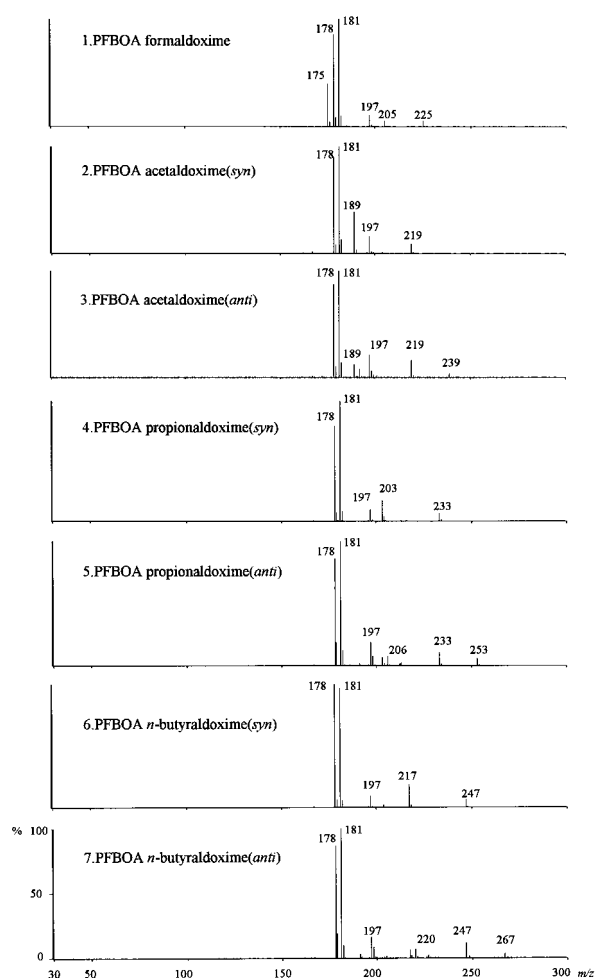


Fig. 5. Negative Ion Chemical Ionization Mass Spectra of PFBOA Aldoximes

of the aldehydes is shown in Fig. 3, while EI and NCI mass spectra of peaks appearing on the TIC chromatogram in Fig. 3 are given in Figs. 4 and 5, respectively.

The EI mass spectra of PFBOA derivatives had a molecular ion (M^+) at m/z 225 for formaldoxime, 239 for acetaldoxime, 253 for propionaldoxime and 267 for *n*-butyraldoxime, respectively. In addition, each PFBOA derivative gave a base fragment peak at m/z 181 ($M - ON=CH-R$)⁺ and a fragment peak ($M - C_6F_5-CH_2$)⁺ at m/z 44 for formaldoxime, 58 for acetaldoxime, 72 for propionaldoxime and 86 for *n*-butyraldoxime.

The NCI mass spectra of formaldoxime, acetaldoxime (*anti*), propionaldoxime (*anti*) and *n*-butyraldoxime (*anti*) gave a molecular ion (M^-) at m/z 225, 239, 253 and 267 respectively. Acetaldoxime (*syn*), propionaldoxime (*syn*) and *n*-butyraldoxime (*syn*) did not give molecular ions, but each PFBOA derivative gave a base fragment peak

at m/z 181 ($M - ON=CH-R$)⁻ and a characteristic fragment peak ($M - HF$)⁻; m/z 205 for formaldoxime, 219 for acetaldoxime, 233 for propionaldoxime and 247 for *n*-butyraldoxime.

Overall, the NCI method was a 'softer' ionization method compared to EI. Fragmentation was simple and produced more peaks that originated from characteristic structures, enabling confirmation of each aldehyde from the spectra obtained after derivatization with PFBOA. In particular, the NCI method is a useful method for the confirmation of compound identity because it reveals characteristic mass spectra. In addition, NCI is a more highly se-

lective detection method than EI because it provides molecularly related ions, specific fragment ions, and allows the monitoring of multiple fragment ions.

Calibration Curves and Detection Limits

The HS-GC/MS (NCI) SIM method showed 5–20 times higher sensitivity than the HS-GC/MS (EI) SIM method, and calibration curves showed linearity (Fig. 6). Detection limits shown in Table 3 were defined according to "Method for determination of tetra- through octa-chlorodibenzo-*p*-dioxins, tetra- through octa-chlorodibenzofurans and coplanar polychlorobiphenyls in industrial water and waste water (JIS K0312)".¹²⁾ Standard deviation was derived from 0.5 $\mu\text{g/l}$ standard solutions of each compound.

Sample Analysis

Concentrations of Aldehydes in Tap Water

Table 4 shows the concentrations of aldehydes in tap water: formaldehyde, 0.7–3.3 $\mu\text{g/l}$; acetaldehyde, N.D.-1.1 $\mu\text{g/l}$; propionaldehyde and *n*-butyraldehyde, below detection limits. Chromatograms of aldehydes in tap water are given in Fig. 7. GC/MS chromatograms of PFBOA derivatives obtained by solvent extraction are known to display a large peak corresponding to PFBOA, which overlaps with the peak of acetaldoxime.²⁾ In contrast, in the chromatogram in Fig. 7 each peak is sharp and clearly defined. Therefore, it is concluded that determination of aldehydes in water by HS-GC/MS (NCI) is rapid, accurate and more highly sensitive than data obtained by solvent extraction-GC/MS.

Concentrations of Aldehydes in Mineral Water

Table 5 shows the concentrations of aldehydes in commercial mineral water. Formaldehyde was detected at the level of N.D.-59 $\mu\text{g/l}$, acetaldehyde, N.D.-260 $\mu\text{g/l}$, propionaldehyde, N.D.-0.9 $\mu\text{g/l}$, and *n*-butyraldehyde, N.D.-0.3 $\mu\text{g/l}$. The maximum observed value for formaldehyde (59 $\mu\text{g/l}$) was close to the Japanese limit of 80 $\mu\text{g/l}$. Some mineral wa-

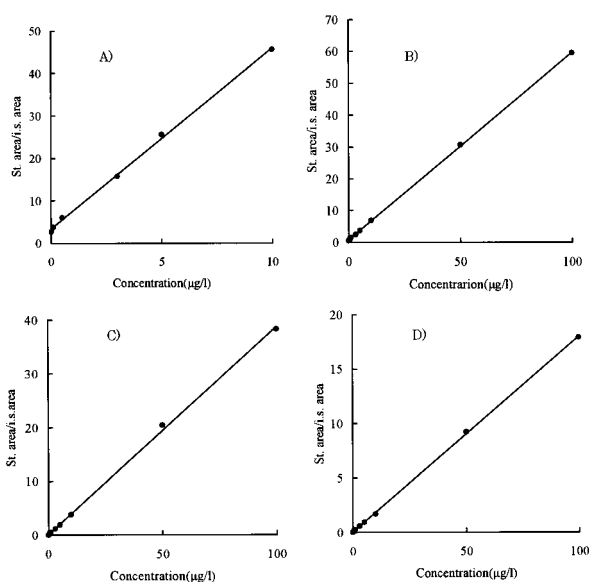


Fig. 6. Calibration Curves for Aldehydes

A) formaldehyde, B) acetaldehyde, C) propionaldehyde, D) *n*-butyraldehyde.

Table 3. Detection Limits

Compound	Determination limit ($\mu\text{g/l}$)
Formaldehyde	0.5
Acetaldehyde	0.5
Propionaldehyde	0.3
<i>n</i> -Butyraldehyde	0.3

Table 4. Aldehyde Concentrations in Tap Water

No.	Concentration ($\mu\text{g/l}$)			
	Formaldehyde	Acetaldehyde	Propionaldehyde	<i>n</i> -Butyraldehyde
1	2.6	1.1	N.D.	N.D.
2	2.3	0.8	N.D.	N.D.
3	0.7	N.D.	N.D.	N.D.
4	3.3	1.1	N.D.	N.D.
5	2.7	1.1	N.D.	N.D.

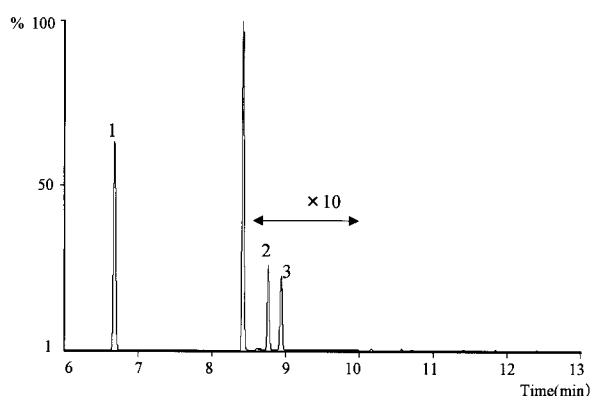


Fig. 7. Typical Chromatogram of Tap Water (NCI)
1. formaldoxime, 2. acetaldoxime (*syn*), 3. acetaldoxime (*anti*).

ters had acetaldehyde concentrations more than 100 times higher than the level in tap water. Hirayama *et al.*²⁾ have suggested that formaldehyde contamination of mineral water is the result of PET bottles use. We detected acetaldehyde in 19 of 24 samples of mineral water contained in PET bottles, but aldehyde concentrations in mineral water bottled in both glass and paper containers were below detectable levels. Of the 19 samples that had detectable levels of acetaldehyde, 13 exceeded 100 $\mu\text{g/l}$. However, five samples (3 French products, 2 Japanese products) that were bottled in PET containers had undetectable concentrations of acetalde-

Table 5. Aldehyde Concentrations in Mineral Water

No.	Source	Bottle	Concentration ($\mu\text{g/l}$)			
			Formaldehyde	Acetaldehyde	Propionaldehyde	<i>n</i> -Butyraldehyde
1	Canada	-	N.D.	0.7	N.D.	N.D.
2	U.S.A.	PET	15	260	N.D.	N.D.
3	U.S.A.	PET	19	143	0.9	0.3
4	U.S.A.	PET	3.8	33	N.D.	N.D.
5	U.K.	PVC	N.D.	N.D.	N.D.	N.D.
6	France	PET	N.D.	N.D.	N.D.	N.D.
7	France	PET	N.D.	N.D.	N.D.	N.D.
8	France	Glass	N.D.	N.D.	N.D.	N.D.
9	France	PET	N.D.	N.D.	N.D.	N.D.
10	U.K.	Glass	N.D.	N.D.	N.D.	N.D.
11	Italy	Glass	N.D.	N.D.	N.D.	N.D.
12	Italy	Glass	N.D.	N.D.	N.D.	N.D.
13	Italy	Glass	N.D.	N.D.	N.D.	N.D.
14	Finland	PET	37	197	0.3	N.D.
15	Japan	-	N.D.	3.1	N.D.	N.D.
16	Japan	PET	25	108	N.D.	N.D.
17	Japan	PET	N.D.	N.D.	N.D.	N.D.
18	Japan	PET	24	155	N.D.	N.D.
19	Japan	PET	N.D.	N.D.	N.D.	N.D.
20	Japan	PET	3.4	17	N.D.	N.D.
21	Japan	PET	19	148	N.D.	N.D.
22	Japan	PET	5.2	109	N.D.	N.D.
23	Japan	PET	25	174	N.D.	N.D.
24	Japan	PET	8	157	N.D.	N.D.
25	Japan	PET	17	200	0.2	N.D.
26	Japan	PET	24	77	N.D.	N.D.
27	Japan	PET	1.3	0.7	N.D.	N.D.
28	Japan	PET	59	147	N.D.	N.D.
29	Japan	PET	34	233	0.2	N.D.
30	Japan	PET	18	225	N.D.	N.D.
31	Japan	Paper	N.D.	N.D.	N.D.	N.D.
32	Japan	PET	5.3	62	N.D.	N.D.
33	Japan	PET	1.7	33	N.D.	N.D.

PET: Polyethylen terephthalate, PVC: Polyvenyl chloride

hyde. This suggests that aldehyde contamination relates to the quality of the container and to the bottling process rather than to the use of PET bottles.

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