Survey of volatile substances in kitchen utensils made from acrylonitrile–butadiene–styrene and acrylonitrile–styrene resin in Japan

Yutaka Abe, Miku Yamaguchi, Motoh Mutsuga, Yoko Kawamura & Hiroshi Akiyama
Division of Food Additives, National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya-ku, Tokyo 158-8501, Japan

Keywords
Acrylonitrile–styrene resin (AS), acrylonitrile–styrene–butadiene resin (ABS), food contact material, kitchen utensil, volatile substance

Abstract
Residual levels of 14 volatile substances, including 1,3-butadiene, acrylonitrile, benzene, ethylbenzene, and styrene, in 30 kitchen utensils made from acrylonitrile–butadiene–styrene resin (ABS) and acrylonitrile–styrene resin (AS) such as slicers, picks, cups, and lunch boxes in Japan were simultaneously determined using headspace gas chromatography/mass spectroscopy (HS-GC/MS). The maximum residual levels in the ABS and AS samples were found to be 2000 and 2800 l g/g of styrene, respectively. The residual levels of 1,3-butadiene ranged from 0.06 to 1.7 l g/g in ABS, and three of 15 ABS samples exceeded the regulatory limit for this compound as established by the European Union (EU). The residual levels of acrylonitrile ranged from 0.15 to 20 l g/g in ABS and from 19 to 180 l g/g in AS. The levels of this substance in seven ABS and six AS samples exceeded the limit set by the U.S. Food and Drug Administration (FDA). Furthermore, the levels of acrylonitrile in three AS samples exceeded the voluntary standard established by Japanese industries. These results clearly indicate that the residual levels of some volatile compounds are still high in ABS and AS kitchen utensils and further observations are needed.

Introduction
Various plastic materials are used in kitchen utensils such as dishes, cups, spoons, forks, measuring cups, and bottles. Acrylonitrile–butadiene–styrene resin (ABS) and acrylonitrile–styrene resin (AS) are two plastics widely used for the production of kitchen utensils because of their heat and impact resistance properties.

ABS and AS are manufactured from the monomers acrylonitrile, styrene, and/or 1,3-butadiene, and unreacted monomers have been detected in food contact materials made from these resins. Furthermore, other volatile substances such as benzene, toluene, 4-vinyl-1-cyclohexene, ethylbenzene, isopropylbenzene, and propylbenzene have also been detected in food contact materials made from these resins (Yoshida et al. 1979; Tan and Okada 1981; Gilbert and Startin 1982; Startin and Gilbert 1984; Tan et al. 1989; Ohno et al. 2002, 2008; Ohno and Kawamura 2010).

Some of these volatile substances have been identified as potentially carcinogenic or toxic. The International Agency for Research on Cancer (IARC) has classified 1,3-butadiene and benzene as group 1 carcinogens (carcinogenic to humans); styrene, acrylonitrile, ethylbenzene, 4-vinyl-1-cyclohexene, and isopropylbenzene as group 2B carcinogens (possibly carcinogenic to humans); methylmethacrylate and toluene as group 3 carcinogens (not
were used. Fifteen samples of ABS kitchen utensils (slicer, pick, peeler, lunch box, spoon, etc.) and 15 samples of AS kitchen utensils (cup, chopsticks, lunch box, plate, bowl, etc.) were purchased from Japanese markets in 2011. For the recovery tests, two ABS sheets (ABS sheet 1 and 2) and two AS sheets (AS sheet 1 and 2) were provided by The Japan Hygienic Olefin and Styrene Plastics Association.

Reagents and standard solutions

N,N-Dimethylacetamide (DMA, high performance liquid chromatography grade) was purchased from Sigma-Aldrich Japan (Tokyo, Japan). Ethanol (for pesticide residue and polychlorinated biphenyl analysis, >99.5%) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

The standards and internal standards used in this study are shown in Table 1. Mixed volatile substance standard stock solutions were prepared at concentrations ranging from 0.5 to 50,000 µg/mL in DMA and ethanol. Mixed internal standard stock solutions were prepared as follows. For the analysis of the residual levels of volatile substances in ABS and AS kitchen utensils, 1,2-butadiene, isobutyronitrile, and p-diethylbenzene were mixed in DMA at 100, 10,000, and 1000 µg/mL. Analysis of the migration levels of these volatile substances was performed using 20% ethanol solution containing the same concentrations.

All standard and internal standard stock solutions were maintained in storage bottles with tightly sealed caps (Kanto Chemical Co. Inc., Tokyo, Japan) and stored at −20°C.

HS-GC/MS conditions

The HS sampler (HP7694; Agilent Technologies, Santa Clara, CA) conditions were as follows. For the determination of residual levels of volatile substances, the oven temperature was held at 90°C for 60 min. The sample loop temperature was at 110°C and transfer-line temperature was 150°C. The injection time was 0.5 min and injection volume was 1.0 mL. Both the sample loop filling time and the sample loop equilibration time were 0.1 min. For the determination of migration levels of volatile substances, the oven temperature was held at 60°C for 30 min. The sample loop temperature was at 80°C and transfer-line temperature was 200°C. The other parameters were same as mentioned above.

The GC/MS (6890 GC and 5973 MSD; Agilent Technologies) conditions were as follows. A DB-624 (0.25 mm i.d. × 60 m, 1.4 µm film thickness; Agilent Technologies) column was used. The oven temperature was initially held at 40°C for 7 min, then increased at 20°C/min to 250°C

Experimental

Samples

In this study, the samples labeled as ABS or AS products were used. Fifteen samples of ABS kitchen utensils (slicer,
and then held at that temperature for 5 min. The injection temperature was 200°C and the transfer-line temperature was 250°C. The helium carrier gas flow rate was constant at 1.2 mL/min. A split injection mode was used with a ratio of 10:1, and the ion source voltage was 70 eV. Finally, the selected ion monitoring (SIM) mode was used, and the monitored ions are given in Table 1.

### Test methods

#### Residual volatile substances

The residual levels of volatile substances in ABS and AS kitchen utensils were determined using a previously reported method (Abe et al. 2013). Each sample (0.5 g) was cut into small pieces and then placed along with 5 mL of a mixed internal standard stock solution in DMA and 2.5 mL of DMA in a 20-mL HS vial, which was immediately tightly sealed. The vial was stored overnight at room temperature and the sample was analyzed via HS-GC/MS after it completely dissolved.

#### Migration of volatile substances

To determine the migration levels of the volatile substances into 20% ethanol, migration tests were performed according to the condition of Japanese official method in the FSL (MHLW). The 20% ethanol (2 mL/cm²) was added to a cut sample and the sample was incubated at 60°C for 30 min. After the incubation, 2 mL of the solution was transferred to a 20-mL HS vial containing 5 μL of the mixed internal standard stock solution in ethanol. The vial was immediately tightly sealed and HS-GC/MS analysis was performed.

### Calibration curves and limits of quantification

To construct calibration curves for determination of the residual levels and migration quantities of the volatile substances, standard solutions were prepared as follows.

For determination of the residual levels of the volatile substances in the ABS and AS kitchen utensils, 5–50 μL quantities of the mixed standard stock solutions in DMA (0.5–50,000 μg/mL) were added to DMA (2.5 mL) in 20-mL HS vials in order to obtain the desired concentrations (0.001–500 μg/mL). Subsequently, 5 μL of mixed internal standard stock solution in DMA was added to each vial and the vials were immediately tightly sealed.

For determination of the quantities of the volatile substances that migrated from the ABS and AS kitchen utensils, 4–20 μL of mixed standard stock solutions in ethanol were added to water (2.0 mL) in 20-mL HS vials in order

### Table 1. Standards and internal standards.

| Chemical name       | CAS No.  | Purity (%) | Supplier¹ | Retention time (min) | Monitor ion (m/z) | Quantifying ion | Qualifying ion |
|---------------------|----------|------------|-----------|----------------------|-------------------|----------------|----------------|
| Standard            |          |            |           |                      |                   |                |                |
| 1,3-Butadiene²      | 106-99-0 | >95        | A         | 6.1                  | 54                | 39, 53         |                |
| Acrylonitrile²      | 107-13-1 | >99.8      | B         | 10.7                 | 53                | 52             |                |
| Benzene             | 71-43-2  | >99        | C         | 13.2                 | 78                | 52             |                |
| Methyl isobutylrate | 547-63-7 | >95        | D         | 13.6                 | 43                | 71, 41         |                |
| Methyl methacrylate | 80-62-6  | >99.8      | E         | 14.1                 | 69                | 41             |                |
| 1-Octene            | 111-66-0 | >95        | D         | 14.9                 | 55                | 70             |                |
| Toluene             | 108-88-3 | >99.5      | F         | 15.0                 | 91                | 92             |                |
| 4-Vinyl-1-cyclohexene | 100-40-3 | >95        | D         | 15.8                 | 79                | 54, 91         |                |
| Ethylbenzene        | 100-41-4 | >99        | D         | 16.3                 | 91                | 106            |                |
| p-Xylene            | 106-42-3 | >98        | D         | 16.4                 | 91                | 106            |                |
| Styrene             | 100-42-5 | >99        | D         | 16.8                 | 104               | 78             |                |
| Isopropylbenzene    | 98-82-8  | >98        | D         | 17.0                 | 105               | 120, 91        |                |
| Propylbenzene       | 103-65-1 | >97        | D         | 17.4                 | 91                | 102, 105       |                |
| α-Methylstyrene     | 98-83-9  | >98        | D         | 17.7                 | 118               | 117, 91        |                |
| Internal standard   |          |            |           |                      |                   |                |                |
| 1,2-Butadiene²      | 590-19-2 | >95        | A         | 7.2                  | 54                | 53, 39         |                |
| Isobutyronitrile    | 78-67-1  | >99        | E         | 13.1                 | 68                | 42             |                |
| p-Diethylbenzene    | 105-05-5 | >99        | D         | 18.3                 | 105               | 117, 120       |                |

¹A, Hayashi Pure Chemical Ind., Ltd.; B, AccuStandard; C, Kokusan Chemical Co., Ltd.; D, Wako pure Chemical Industries Ltd.; E, Tokyo Chemical Industry Co., Ltd.; F, Aldrich Chemical Co., Inc.
²Methanol solution (1000 μg/mL).
to obtain the desired concentrations (1–50 ng/mL). Subsequently, 5 μL of mixed internal standard stock solution in ethanol was added, and the vials were immediately tightly sealed.

The prepared standard solutions in the HS vials were analyzed using HS-GC/MS, and calibration curves were constructed by plotting the peak area ratios for 1,3-butadiene versus 1,2-butadiene, for acrylonitrile versus isobutyronitrile, and for the other volatile substances versus p-diethylbenzene.

The limit of quantification (LOQ) was defined for all of the volatile substances as a signal-to-noise ratio (S/N) of 10/1 for the peak intensity.

**Recovery test**

To evaluate the accuracy of the method for determining residual volatile substances in the ABS and AS samples, recovery tests were performed. The mixed standard stock solutions were spiked with two ABS sheets and two AS sheets. The analytes other than styrene and ethylbenzene were spiked at levels equivalent to 0.5 and 2 μg/g. Styrene and ethylbenzene were spiked at levels equivalent to 50 and 250 μg/g because the residual levels of styrene and ethylbenzene in the sheets were high (approximately 50–2000 μg/g).

**Results and Discussion**

**Assessment of the method for the determination of residual volatiles**

Previously, we developed a method for the simultaneous determination of the residual levels of various volatile substances in ABS toys and assessed the linearity, accuracy, and precision of this method (Abe et al. 2013). In this study, the application of this method to determine the residual levels of volatiles in ABS and AS kitchen utensils was investigated. To assess the linearity of the method, calibration curves for 14 volatile substances were constructed using DMA as the sample solvent. Good linearity was achieved over the concentration ranges 0.005–10 μg/mL for 1,3-butadiene and acrylonitrile, 0.025–500 μg/mL for isopropylbenzene, and 0.01–500 μg/mL for the other volatile substances. The correlation coefficients (R²) for all of the volatile substances were >0.998. The LOQs for the residual volatile substances in the ABS and AS kitchen utensils were estimated to be 0.025 μg/g for 1,3-butadiene and acrylonitrile, 0.13 μg/g for isopropylbenzene, and 0.05 μg/g for the other volatile substances.

To assess the accuracy and precision of this method, recovery tests were performed in triplicate (Table 2). The recovery rates for the volatile substances found in ABS and AS sheets ranged from 88% to 108%, and the relative standard deviation (RSD) values were in the range from 1% to 6%. Because the residual levels of methylmethacrylate and 4-vinyl-1-cyclohexene in ABS sheet 1 were greater than the 0.5 or 2 μg/g spiking levels, these recoveries and RSD values were not tested. However, when these volatiles were spiked at concentrations of 50 and 250 μg/g, recovery rates and RSD values were all in the range from 97% to 104% and from 1% to 4%, respectively. Consequently, acceptable linearity, recovery rates, and RSD values were obtained for all of the substances, suggesting that this method is reliable for the quantitative determination of the amounts of volatile substances in ABS and AS kitchen utensils.

**Residual levels of volatile substances in ABS kitchen utensils**

Residual levels of the volatile substances in 15 ABS kitchen utensils are shown in Table 3. Eleven volatile substances were detected.
substances, including 1,3-butadiene, acrylonitrile, and benzene, were detected in all of the kitchen utensil samples examined in this study. Notably, the residual levels of ethylbenzene and styrene were in the range from 30 to 960 and 110 to 2000 μg/g, respectively, and were significantly higher than those of the other detected substances. In addition, methylmethacrylate, 4-vinyl-1-cyclohexene, and α-methylstyrene were present at reasonably high concentrations of 0.23–250, 0.16–320, and 0.28–100 μg/g, respectively. The residual levels of the remaining volatile substances were <50 μg/g. These results indicate that the residual levels of these 14 volatile substances in the 15 kitchen utensils made from ABS are similar to those in the previously evaluated ABS toys (Abe et al. 2013).

The total residual levels of five volatile substances (toluene, ethylbenzene, styrene, isopropylbenzene, and propylbenzene) regulated in Japan for PS kitchen utensils ranged from 190 to 2100 μg/g (average: 910 μg/g). These levels were less than the regulatory limit for PS kitchen utensils as established in the Japanese FSL (5000 μg/g). However, the residual levels of 1,3-butadiene detected in three of the 15 samples exceeded the EU regulatory limit (1 mg/kg) and those of acrylonitrile in seven of the 15 samples exceeded the U.S. FDA limit (11 μg/g).

Historically, the residual levels of acrylonitrile in ABS kitchen utensils in Japan were 0–138 μg/g (Yoshida et al. 1979) and 0.3–50.4 μg/g (Ohno and Kawamura 2010). The present results are similar to the results reported in 2010. In addition, the total residual level of the five volatile substances regulated for PS kitchen utensils in Japan ranged from 100 to 10,320 μg/g (average: 1900 μg/g) in 1979. Thus, the total residual levels of these five volatile substances in this study were significantly lower than those reported in 1979.

### Residual levels of volatile substances in AS kitchen utensils

Residual levels of the volatile substances in 15 AS kitchen utensils are shown in Table 4. Seven volatile substances, including acrylonitrile, toluene, and ethylbenzene, were detected in all 15 samples and benzene and α-methylstyrene were detected in some of the samples. The 1,3-butadiene, methlysobutyrat, methylmethacrylate, 1-octene, and 4-vinyl-1-cyclohexene were not detected in any of the AS kitchen utensils. However, residual levels of ethylbenzene and styrene ranged from 76 to 1000 and 430 to 2800 μg/g, respectively, which were significantly higher than those of the others substances, followed by toluene and acrylonitrile with concentrations ranging from 0.43 to 570 and 20 to 180 μg/g, respectively. The residual levels of the remaining volatile substances were <50 μg/g. These results suggest that the residual levels of acrylonitrile, ethylbenzene, and styrene in AS kitchen utensils are greater than those in ABS kitchen utensils, whereas those of α-methylstyrene in kitchen utensils made from AS are lower than those in kitchen utensils made from ABS.

The total residual levels of five volatile substances (toluene, ethylbenzene, styrene, isopropylbenzene, and propylbenzene) regulated in Japan for PS kitchen utensils were 830–3200 μg/g (average: 1700 μg/g) and fell below the regulatory limit for volatile substances in PS kitchen utensils as established in the Japanese FSL (5000 μg/g).

### Table 3. Residual levels of 14 volatile substances in ABS kitchen utensils.

| Sample | 1,3-BD | AN | BZ | MiB | MMA | 1OC | TO | 4-VC | EB | XYL | ST | IPB | PB | α-MST |
|--------|--------|----|----|-----|-----|-----|----|-----|----|-----|----|-----|----|--------|
| ABS1   | 0.59   | 4.4| 0.10| NQ  | NQ  | 0.49| 0.34| 2.0 | 85 | 1.4 | 120| 2.7 | 1.7 | 6.5    |
| ABS2   | 0.69   | 3.8| 0.07| NQ  | NQ  | 0.34| 0.29| 1.5 | 75 | 0.78| 110| 2.8 | 1.5 | 4.5    |
| ABS3   | 0.10   | 15 | 0.28| NQ  | 0.23| 0.74| 0.49| 180| 11 | 750| 22  | 7.6 | 6.9    |
| ABS4   | 0.39   | 12 | 0.64| NQ  | 1.8 | 1.1 | 22  | 260| 13 | 920| 30  | 20  | 1.2    |
| ABS5   | 0.97   | 0.55| 0.69| 4.2 | 200 | 0.37| 2.6 | 1.8 | 750| 28  | 330| 13  | 6.7 | 0.35   |
| ABS6   | 1.2    | 1.8 | 0.79| 8.1 | 250 | 0.30| 3.3 | 1.4 | 960| 17  | 440| 15  | 10  | 0.28   |
| ABS7   | 0.20   | 20 | 0.05| NQ  | 18  | 0.40| 21  | 70  | 29 | 990| 18  | 7.1 | 46    |
| ABS8   | 0.21   | 14 | 0.05| NQ  | 21  | 0.24| 10  | 83  | 9.8| 800| 15  | 7.5 | 97    |
| ABS9   | 0.36   | 7.6 | 0.11| NQ  | 0.21| 0.60| 7.7 | 190| 3.1| 460| 9.9 | 4.0 | 68    |
| ABS10  | 0.79   | 6.9 | 0.20| NQ  | 0.81| 4.9 | 5.6 | 160| 2.0| 210| 8.3 | 2.8 | 16    |
| ABS11  | 0.73   | 13 | 0.12| NQ  | 0.77| 66  | 30  | 1.9| 660| 14  | 3.0 | 100   |
| ABS12  | 1.3    | 0.71| 0.36| 7.0 | 200 | 0.30| 2.8 | 2.2 | 630| 10  | 290| 7.7 | 0.40  |
| ABS13  | 1.7    | 11 | 0.12| NQ  | 1.5 | 1.9 | 320 | 46  | 4.2| 2000| 31 | 4.8 | 17    |
| ABS14  | 0.06   | 0.15| 0.12| NQ  | 0.60| 0.49| 2.3 | 0.16| 120| 6.6 | 350| 23  | 19   | 0.98  |
| ABS15  | 0.62   | 13 | 0.84| NQ  | 1.6 | 28  | 260 | 12  | 900| 27  | 19  | 0.68  |
| LOQ    | 0.025  | 0.025| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05 | 0.13 | 0.05 | 0.05 |

Mean of two trials (μg/g), NQ = not quantified (Under the LOQ). ABS, acrylonitrile–butadiene–styrene resin.
However, the residual levels of acrylonitrile in three out of the 15 AS samples exceeded the voluntary standard set by Japanese industries (80 μg/g). Moreover, those in six and three out of the 15 AS samples exceeded the U.S. FDA limits (50 and 80 μg/g, respectively).

Yoshida et al. (1979) reported that the residual levels of acrylonitrile in 79 AS kitchen utensils obtained from Japanese markets ranged from 4 to 376 μg/g, and Ohno and Kawamura (2010) reported that those in five Japanese AS kitchen utensils ranged from 16.8 to 54.5 μg/g.

The present results are thus similar to those reported in 2010. In 1979, total residual levels of the five volatile substances regulated for PS kitchen utensils in Japan ranged from 560 to 7390 μg/g (average: 2600 μg/g). Clearly, the total residual levels of these five volatile substances obtained in this study are significantly lower than those reported in 1979.

Differences in the residual levels of volatile substances found in 1979 and this study for ABS and AS kitchen utensils can be attributed to an improvement in the quality of the materials due to more complete polymerization, which has been achieved through advances in manufacturing technology and the adoption of increasingly strict EU regulations.

### Migration levels from ABS and AS kitchen utensils

To determine migration levels of volatile substances from ABS and AS kitchen utensils, migration tests were performed using a food simulant. ABS and AS kitchen utensils are typically used for common foods, while they are occasionally used for fatty foods. In the case of common foods, water is used as the simulant in Japan, whereas 10% ethanol is used in the U.S. and EU. For more effective migration of fat-soluble substances into the solvent, thus the migration tests were performed at 60°C for 30 min. This condition refers to the official method of plastic migration test in Japanese FSL (MHLW).

To assess the linearity of determining the migration of volatile substances, calibration curves were constructed using 20% ethanol as the sample solvent. Good linearity was achieved over the concentration range from 3 to 50 ng/mL for all of the volatile substances, and $R^2$ was >0.994 for all of them. The LOQs for the quantities of

### Table 4. Residual levels of 14 volatile substances in AS kitchen utensils.

| Sample | 1,3-BD | AN | BZ | MIB | MMA | 1-OC | TO | 4-VC | EB | XYL | ST | IPB | PB | α-MST |
|--------|--------|----|----|-----|-----|------|----|------|----|-----|----|-----|----|-------|
| AS1    | NQ     | 160| 0.61| NQ  | NQ  | NQ   | 570| NQ   | 120| 12  | 2000| 26  | 18 | 0.09  |
| AS2    | NQ     | 28 | 0.36| NQ  | NQ  | NQ   | 1.4 | NQ   | 1000| 6.4 | 720 | 17  | 12 | 0.23  |
| AS3    | NQ     | 23 | 0.36| NQ  | NQ  | NQ   | 1.5 | NQ   | 1000| 5.8 | 670 | 15  | 12 | 0.16  |
| AS4    | NQ     | 23 | NQ  | NQ  | NQ  | NQ   | 0.51| NQ   | 400 | 4.1 | 570 | 15  | ND |       |
| AS5    | NQ     | 19 | NQ  | NQ  | NQ  | NQ   | 0.78| NQ   | 76  | 0.32| 1900| 6.3 | 4.3| 0.57  |
| AS6    | NQ     | 47 | NQ  | NQ  | NQ  | NQ   | 0.57| NQ   | 200 | 21  | 1100| 15  | 18 | 0.44  |
| AS7    | NQ     | 54 | 0.22| NQ  | NQ  | NQ   | 1.3 | NQ   | 590 | 6.4 | 520 | 7.9 | 6.0| 0.27  |
| AS8    | NQ     | 21 | 0.33| NQ  | NQ  | NQ   | 1.5 | NQ   | 800 | 4.8 | 690 | 14  | 10 | NQ    |
| AS9    | NQ     | 54 | 0.25| NQ  | NQ  | NQ   | 2.8 | NQ   | 640 | 4.8 | 600 | 10  | 7.5| 0.14  |
| AS10   | NQ     | 20 | 0.34| NQ  | NQ  | NQ   | 1.4 | NQ   | 1000| 4.9 | 700 | 8.4 | 7.4| 0.31  |
| AS11   | NQ     | 43 | NQ  | NQ  | NQ  | NQ   | 0.43| NQ   | 180 | 16  | 990 | 13  | 15 | 0.28  |
| AS12   | NQ     | 55 | 0.27| NQ  | NQ  | NQ   | 1.2 | NQ   | 650 | 4.9 | 630 | 11  | 7.6| 0.33  |
| AS13   | NQ     | 180| 0.53| NQ  | NQ  | NQ   | 0.80| NQ   | 250 | 11  | 2800| 68  | 46 | 1.3   |
| AS14   | NQ     | 150| 0.54| NQ  | NQ  | NQ   | 1.5 | NQ   | 200 | 13  | 2700| 57  | 40 | 0.73  |
| AS15   | NQ     | 21 | NQ  | NQ  | NQ  | NQ   | 0.89| NQ   | 450 | 3.5 | 430 | 5.5 | 3.2| NQ    |
| LOQ    |       | 0.025| 0.025| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05| 0.05| 0.13| 0.05| 0.05 |

Mean of two trials (μg/g), NQ = not quantified (Under the LOQ). AS, acrylonitrile–styrene resin.

### Table 5. Migration amounts of volatile substances from ABS and AS kitchen utensils.

| Sample | MMA | EB | XYL | ST | Sample | AN | EB | ST |
|--------|-----|----|-----|----|--------|----|----|----|
| AB51   | NQ  | NQ | NQ  | NQ | AS1    | 18 | NQ | 46 |
| AB52   | NQ  | NQ | NQ  | NQ | AS2    | NQ | 12 | 16 |
| AB54   | NQ  | NQ | NQ  | 34 | AS3    | NQ | 14 | 16 |
| AB56   | 16  | 12 | NQ  | 12 | AS4    | NQ | 8  | 10 |
| AB57   | NQ  | NQ | NQ  | 8  | AS5    | NQ | NQ | 32 |
| AB58   | NQ  | NQ | NQ  | 30 | AS6    | NQ | NQ | 22 |
| AB59   | NQ  | 6  | 6   | 16 | AS7    | NQ | NQ | 8  |
| AB511  | NQ  | NQ | 46  | 40 | AS8    | NQ | 14 | 18 |
| AB512  | 16  | 22 | 30  | 16 | AS12   | NQ | 6  | 10 |
| AB513  | NQ  | NQ | NQ  | 76 | AS15   | NQ | NQ | 8  |
| LOQ    | 6   | 6  | 6   | 6  | NQ     | NQ | NQ | 8  |

Mean of two trials (ng/cm²), NQ = not quantified (Under the LOQ). ABS, acrylonitrile–butadiene–styrene resin; AS, acrylonitrile–styrene resin.
the volatile substances that migrated into 20% ethanol from ABS and AS kitchen utensils were estimated to be 6 ng/cm² for all of the volatile substances.

As shown in Table 5, migration levels of the volatiles in 10 of the 15 ABS samples and 10 of the AS samples into 20% ethanol at 60°C for 30 min were determined using HS-GC/MS. Methylmethacrylate, ethylbenzene, xylene, and styrene from the ABS samples and acrylonitrile, ethylbenzene, and styrene from the AS samples were detected in the simulant. Styrene was detected in the simulant for all but two ABS samples because of its high residual levels. The quantities of volatile substances that migrated into the simulant ranged from 6 to 76 ng/cm².

The migration levels of styrene correlated well with the residual levels \( r = 0.8710 \) in ABS kitchen utensils and \( r = 0.9320 \) in AS kitchen utensils, Fig. 1). The slope of the ABS regression line (0.0174) was greater than that of the AS regression line (0.0093). In addition, xylene migrated only from the ABS samples. These results suggest that the migration levels for styrene and xylene from the ABS samples were higher than those from the AS samples, which might be attributed to the softness of ABS.

It should be noted that the European Standard suggests that volatile substances can readily migrate from the cut edges of ABS and AS kitchen utensils (European Standard EN 13130-1:2004, 2004). Therefore, the accurate assessment of the migration of volatile substances from the surfaces of kitchen utensils, other than from cut edges, is difficult; thus, the actual migration level into foods might be lower than those reported in this study.

Acrylonitrile, styrene, and ethylbenzene, which were detected in the above described migration tests, are classified as group 2B carcinogens by IARC. Although it is possible that these compounds migrate from kitchen utensils into foods, there currently are no regulations for 1,3-butadiene and styrene in the Japan FSL. Regulatory limits for these volatiles are therefore required in Japan in order to ensure the safety of food contact materials.

Conclusion

Residual levels of 14 volatile substances in ABS and AS kitchen utensils in Japan were determined using HS-GC/MS. All 14 volatile substances were detected in the ABS kitchen utensils and nine volatile substances were found in the AS samples. Although the residual levels of acrylonitrile and 1,3-butadiene were lower than those reported over 30 years ago, those residual levels exceeded the Japanese voluntary standard and the regulatory limits established in the U.S. and EU in some kitchen utensils. In addition, the residual levels of ethylbenzene and styrene were found to be >1000 µg/g in some samples. Therefore, the results of this study are very important for ensuring the safety of food contact materials made from ABS and AS and indicate that further study is needed.

Acknowledgments

We are grateful to Hiroyuki Ohno (Nagoya City Public Health Research Institute) for his helpful advice and the Japan Hygienic Olefin and Styrene Plastics Association for providing sheet samples for the recovery tests. This study was partly supported by a grant from the Ministry of Health, Labour and Welfare, Japan.

Conflict of Interest

None declared.

References

Abe, Y., M. Yamaguchi, M. Mutsuga, H. Akiyama, and Y. Kawamura. 2013. Volatile substances in polymer toys made from butadiene and styrene. Am. J. Anal. Chem. 4:229–237.

European Commission. 2011. COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. Off. J. Eur. Union L 21:1–89.
European Standard EN 13130-1:2004. 2004. Materials and articles in contact with food stuffs. 1-62.
Gilbert, J., and J. R. Startin. 1982. Determination of acrylonitrile monomer in food packaging materials and in foods. Food Chem. 9:243–252.
International Agency for Research on Cancer. 2013. "IARC monographs on the evaluation of carcinogenic risks to humans". Available at http://monographs.iarc.fr/ENG/Classification/index.php. (accessed 3 February 2014).
Ministry of Health, Labour and Welfare. 2014. Ministry of Health, Labour and Welfare, the Japanese Food Sanitation Law. Available at http://www.mhlw.go.jp/file/06-Seisakujouhou-11130500-Shokuhinanzenbu/0000035338.pdf. (in Japanese, accessed 3 February 2014).
Ohno, H., and Y. Kawamura. 2010. Analysis of acrylonitrile, 1,3-butadiene, and related compounds in acrylonitrile-butadiene-styrene copolymers for kitchen utensils and children’s toys by headspace gas chromatography/mass spectrometry. J. AOAC Int. 93:1965–1971.
Ohno, H., M. Suzuki, T. Aoyama, and K. Mizutani. 2002. Survey of residual substances in polystyrene and styrene copolymer products for kitchen utensils and food containers. Annu. Rep. Nagoya City Public Health Res. Inst. 48:61–65.
Ohno, H., M. Suzuki, and M. Nakajima. 2008. Survey of residual volatile substances in acrylonitrile-butadiene-styrene copolymer and polystyrene toys. Annu. Rep. Nagoya City Public Health Res. Inst. 54:58–61.
Startin, J. R., and J. Gilbert. 1984. Single ion monitoring of butadiene in plastics and foods by coupled mass spectrometry-automatic headspace gas chromatography. J. Chromatogr. 294:427–430.
Tan, S., and T. Okada. 1981. Determination of residual 1,3-butadiene in synthetic resins containing butadiene. J. Food Hyg. Soc. Japan 22:50–154.
Tan, S., T. Tatsuno, and T. Okada. 1989. Selected-ion monitoring of 4-vinyl-1-cyclohexene in acrylonitrile-butadiene-styrene polymer products and food simulants. J. Chromatogr. 482:246–251.
U.S. Food and Drug Administration. 2013a. Indirect food additives: polymers. 21 CFR 177.1020.
U.S. Food and Drug Administration. 2013b. Indirect food additives: polymers. 21 CFR 177.1040.
Yoshida, R., Y. Watanabe, K. Sato, and F. Endo. 1979. Survey of residual acrylonitrile monomer in AS and ABS resin food containers. Annu. Rep. Tokyo Metrop. Res. Lab. Public Health 30:63–166.