Determination of Bromide Ions in Food by Unsuppressed Ion Chromatography with Ultraviolet Detection after Microwave Digestion in a Sealed PTFE Vessel

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A residue procedure for bromide ion was studied to establish an analytical method using ion-exchange chromatography with an ultraviolet spectrometric detector. Samples were prepared by a microwave digestion and cation-exchange removal of sodium ions. The procedure is very simple and quick (ashing time is a few minutes). Recoveries of bromide ions ranged from 87 to 119% at 25 and 50 ppm. Several samples for a total diet study were also examined.

INTRODUCTION

We have been studying artificial contaminants in food and have proposed several methods of assaying pesticides in foods (Miyahara et al., 1991, 1992a,b, 1993a,b). Foods contain inorganic bromide at some levels which depend on the nature of the foodstuffs. Drinking water of specific volcanic ash areas in Japan and some marine products (sea plants) are known as natural bromine sources for human intake. Some plants (carrot, tobacco, tomato, celery, and melon) accumulate bromide (Kabata-Pendias and Pendias, 1992). When crops have been grown in soil fumigated by methyl bromide, they contain much more inorganic bromide than those raised in unfumigated soil (Grave and Grevenstuk, 1979; Yukita and Komamura, 1986). Some inorganic bromide in crops is considered to be a breakdown product of brominated fumigants which are used to control pests in harvested crops (Shrader et al., 1942; Yukita and Komamura, 1986; Zurer, 1993). Residual bromide levels are usually higher in such foods than in unfumigated products (Kabata-Pendias and Pendias, 1992). Many have focused upon inorganic bromide, because of the high daily intake from food and drinking water. To estimate dietary intake of bromide and determine levels in food, a simple and rapid analytical procedure is needed to analyze many samples.

Several analytical methods of measuring inorganic bromide in food have been used for official procedures (FDA, 1993; OVR, 1988; DFG, 1987). The methods include: volumetric determination of grains at a level of 0.25 ppm (FDA, 1993; Kolthoff and Yutzy, 1942; Shrader et al., 1937), gas chromatographic determination of vegetables at a level of 1–5 ppm (DFG, 1987; Grave and Grevenstuk, 1979), and colorimetric determination (AOAC, 1990; Momokawa et al., 1981) of fish products (kamaboko) and bread at a level of 2.5 ppm. These methods involve a chain reaction involving bromine and/or a derivation of the bromide. This causes erroneous results owing to chloride and other coexisting ions. To overcome such problems, direct determination methods for bromide have been developed recently (APHA, 1992a). Ion pair liquid chromatography and ion chromatography have been used to determine inorganic bromine with traditional ashing procedures (OVR, 1987; Taguchi et al., 1992), which are simple and precise.

Basically, the ashing process is important for the determination of bromide in food. Ashing at 550 °C weighs with determination of bromide because this process converts the chemical forms of bromine to bromide in the sample with oxidants.

$$2BrO_3^- \xrightarrow{>450\ °C} 2Br^- + 3O_2$$

However, these methods were established over 50 years ago (Kolthoff and Yutzy, 1937). Some modifications have been proposed, but the essential principle remains the same. The ashing requires exposure to molten sodium hydroxide, and losses are easily incurred because of ignition or violent boiling. A new technology for ashing that uses a microwave oven has been developed for metals in biological samples (APHA, 1992b; White, 1988; Isoyama et al., 1990).

To reduce analytical time and costs and to obtain reproducible results, we propose a new digestion procedure using the microwave oven that will replace the traditional ashing and discuss ion chromatographic determination with a UV detector.

EXPERIMENTAL PROCEDURES

Apparatus. (*a*) *The instruments* consisted of a Tosoh Model CCPM pump for high-performance liquid chromatography with a UV spectrophotometric detector (Hitachi Model 655 UV–visible monitor, which was operated at 205 nm), an autosampler (Tosoh Model AS8020), a degasser (Tosoh Model SD8022), and a column oven (Tosoh Model CO8010). An anion-exchange column (32 mm × 4.6 mm i.d.) with a polar polymer [6 μm; TSKGel IC-Anion-PWXL (Tosoh Co.)] was used with a phosphate buffer (2.5 mM potassium dihydrogen phosphate and 1 mM potassium hydrogen phosphate) as a mobile phase at 1 mL/min. The column oven was maintained isothermally at 40 °C. A 10-μL injection in the full presuction mode was utilized. Data were processed with a Shimadzu Model CR5A data processor.

(*b*) *A Hitachi Model MRO-G6 microwave oven* was used to digest sample with a sealed PTFE vessel. A sample was heated at 100 W on turntable and at 200 W without power correction.

(c) A *PTFE vessel kit* (San'ai Kagaku Co., Nagoya) was used to ash a sample (Figure 1).

(*d*) *An Ikeda Rika Model muffle* MPF-400 and nickel vessel were used to ash a sample at 550 °C.

Reagents and Other Materials. (*a*) *Anion standards* included potassium bromide >99.5%, potassium chloride >99.5%, potassium iodide >99.5%, and potassium nitrite >99%. These were purchased from E. Merck, Germany.

(*b*) *All inorganic reagents* for analysis were of Japanese Industrial Standards (JIS) extra pure grade. These may be compatible with ACS grade. Water was of HPLC grade (Ciba Merck, Co.).

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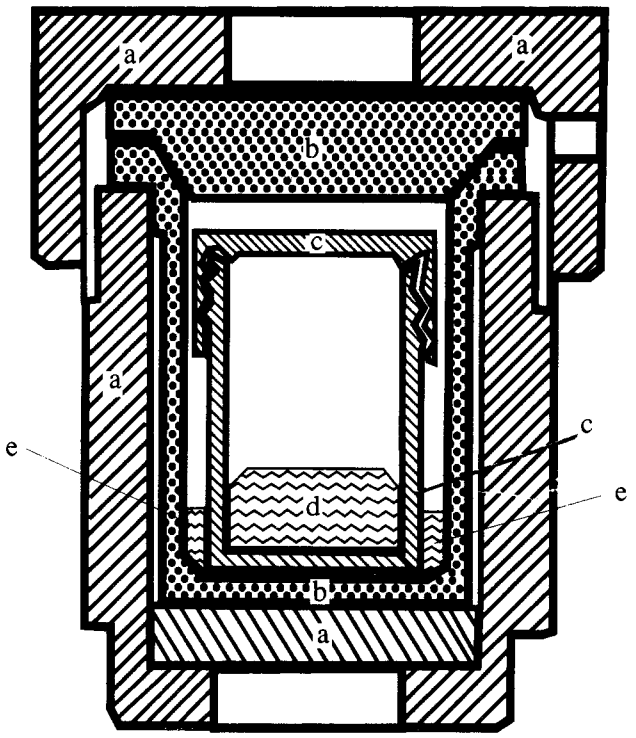

Figure 1. Sealed PTFE vessel for microwave digestion: (a) polypropylene jacket; (b) PTFE pressure vessel (25-mL capacity); (c) Teflon PFA interior vessel (7-mL capacity); (d) sample, alkaline, and peroxide mixture; (e) 0.5 mL of water.

(c) *Cation-exchange resin* (Toyo Pearl 650M, Tosoh Co.) was used for decationization. The crude resin was washed with water, methanol, and finally 0.5 N sulfuric acid for activation of the active sites.

(d) *Solid-phase extraction (SPE)* (Sep-Pak C_{18}, Waters Co.) was used for decolorization. The Sep-Pak was washed with 5 mL of methanol and 5 mL of water before use.

(e) *Membrane filters* of 0.5 and 1.2 μm (Sample Prep SJCN013NS and Ultra Free UFC30LH00, Millipore Co.) were used for sample filtration. The filters were washed with water (10 mL) before use.

Samples. Total diet samples were prepared by the Osaka Prefecture Institute of Hygienic Sciences in 1990 and 1991. Samples for recovery tests were obtained from retail stores in Tokyo. Commodity classes of total diet study are groups I (rice), II (grains, potatoes, and their products), III (sweeteners, candies, and cakes), IV (fat and oil), V (beans and their products), VI (fruits), VII (leafy vegetables), VIII (root and fruit vegetables), IX (flavors and beverages), X (fish, shell fish, and their products), X (meat, eggs, and their products), XII (milk and dairy products), and XIII (spices and their products).

Sample Preparation. A 50-g sample was ground thoroughly in a homogenizer. The ground sample (100 mg) was placed in an interior FEP vessel, and 0.5 mL of 0.5 N sodium hydroxide was added to the sample. Water (0.5 mL) was poured into the outer reactor pressure PTFE vessel. The interior vessel was set in the PTFE vessel. Then the pressure vessel was tightly sealed with a polypropylene jacket using a wrench. The water in the pressure vessel could serve to compensate for the rise in the inner pressure. The schematic diagram of microwave digestion vessel is shown in Figure 1. A set of two vessels was located symmetrically on the turntable of a microwave oven. These samples were heated together with a beaker of 50 mL of water placed in the center of the turntable for 2 min, at a power setting corresponding to 100–200 W. After the beaker was removed, the sample was heated again for 2 min. After cooldown, 100–200 μL of 30% hydrogen peroxide was added to the partially digested sample and the mixture was allowed to stand until the reaction ceased. The sample was sealed again as before and heated in a microwave oven for 2 min at 200 W. The digested sample was eluted through a cation-exchange resin column to lower the pH value of the solution by the removal of sodium ions. The pH value of the sample was adjusted from 2 to 4 and was monitored using a small piece of universal pH indicator. To reduce interferences, if necessary, the eluate was passed through a Sep-Pak C_{18}, 1.5 mL of water was passed through the column, and the eluates were combined. The sample was filtered through 0.5- and 1.2-μm filters, and then the volume was adjusted to 1.5 mL. Ten microliters of the sample was injected as described under Apparatus.

Ashing with Muffle Furnace at 550 °C. Potassium bromide (100 μg) was heated with sodium hydroxide (10 mg) at 550 °C for 6, 20, and 28 h. The nickel vessels were washed with 50 mL of water after cooldown, and the water was removed by heating. The samples were dissolved in 1 mL of water and analyzed as described in the text.

RESULTS AND DISCUSSION

Analytical Conditions. Ion chromatography columns vary among suppliers with respect to the ion-exchange functional groups, ion-exchange capacity, particle pore size, and particle size. To determine which would be most suitable for our study, the four columns listed in Table 1 were examined, including an ODS column for ion pair chromatography. Parameters of the calibration curves for bromide and three anions (nitrite, nitrate, and iodide) are shown in Table 1. We found that the Tosoh TSKGel was most suitable for our study, since the slope value was the largest and the retention times were short with sufficient separation. Those characteristics are required because there would be several univalent ions in the sample and, after analysis, the column has to be purged of retentive ions for a long time before the next analysis. The intercept value for Shimadzu Shim Pak A1 was rather large because of bleeding. The Showa Denko IC I524A column performed well, but the analytes were retained longer because it has a greater ion-exchange capacity.

The sensitivity and reproducibility of ion pair chromatography were good, but it was difficult to separate reverse peaks which frequently appeared from the bromide peak. Thus, the Tosoh TSKGel was used for our study.

The mobile-phase pH effects on analyte separation were examined by changing the ratios of 5 mM disodium hydrogen phosphate and 5 mM sodium dihydrogen phosphate solution. As shown in Figure 2, analytes, particularly iodide, were retained longer as the pH value of the mobile phase was lowered. The shapes of the peaks also changed. At pH 8.28 (5 mM disodium hydrogen phosphate), bromide was not separated from other ions. On the other hand, at pH 5.65 (5 mM sodium dihydrogen phosphate), all of the peaks spread and were too broad to determine the areas. The peak of iodide was not observable under the conditions because it may be too retentive.

The effects of the mobile-phase pH on peak intensity were examined by changing the ratio of 5 mM disodium hydrogen phosphate and 5 mM sodium dihydrogen phosphate. As shown in Figure 3, all intensities were reduced as the pH value was lowered. The graph indicates the relative intensity based upon the intensity at pH 8.28. These results show that the intensities at pH 5.65 are from half to one-fourth of those at pH 8.28. The cutoff value for nitrite, bromide, and nitrate was pH 6.81. At this point, they may change their chemical forms in the solution. Thus, daily calibration of these ions is required.

Digestion with a Microwave Oven vs Ashing with a Muffle Furnace. Traditional ashing with a muffle furnace requires a long time (over 15 h), so we tested a microwave digestion procedure, which was quite simple. The sample was microwaved with 0.5 N sodium hydroxide and hydrogen peroxide for a few minutes at 200 W. Vegetables, fruits, meat, and related products were suitably digested. However, oily products and bread were difficult

Table 1. Experimental Parameters for Calibration Curves[a] Comparing Ion Chromatographic Columns

column	parameter	nitrite	bromide	nitrate	iodide
Tosoh[b]	mode (ion chromatography)				
	range (μg)	0.1–0.5	0.1–0.5	0.1–0.5	0.1–0.5
	correl coeff	0.995	0.995	0.996	0.995
	intercept	−700	−713	−882	179
	slope	81	63	82	16
	b/*a*	−8.2	−11	−11	−11
	av elution time (min)	3.15	3.86	4.98	12.69
	CV% for the elution time	0.93	1.1	1.3	1.6
Shimadzu[c]	mode (ion chromatography)				
	range (μg)	0.1–0.5	0.1–0.5	0.1–0.5	0.1–0.5
	correl coeff	0.994	0.994	0.994	0.984
	intercept	806	459	605	146
	slope	50	38	49	9
	b/*a*	16	12	12	17
	av elution time (min)	5.09	6.02	7.55	18.25
	CV% for the elution time	1.2	1.0	0.9	1.8
Shoden[d]	mode (ion chromatography)				
	range (μg)	0.1–0.5	0.1–0.5	0.1–0.5	0.1–0.5
	correl coeff	0.999	0.999	0.999	0.997
	intercept	198	114	16	32
	slope	37	26	31	5
	b/*a*	5.3	4.3	0.5	6.5
	av elution time (min)	3.77	4.58	5.96	15.39
	CV% for the elution time	0.14	0.25	0.28	0.65
Shiseidoh[e]	mode (ion pair HPLC)				
	range (μg)	0.1–0.5	0.1–0.5	0.1–0.5	0.1–0.5
	correl coeff	0.990	0.992	0.993	0.991
	intercept	214	245	253	291
	slope	103	148	226	155
	b/*a*	2.1	1.7	1.1	1.9
	av elution time (min)	1.66	1.92	2.68	7.01
	CV% for the elution time	0.33	0.23	0.17	0.064

[a] The HPLC conditions were as described in the text except for the columns. [b] Tosoh, TSKGel IC Anion-PWXL, 6 μm, 3.5 cm × 4.6 mm i.d., 30 μequiv/mL, polyvinylate base. [c] Shimadzu, Shim-Pak A1, polyacrylate base, 12.5 μm, 50 μequiv/g, 10 cm × 4.6 mm i.d. [d] Showa Denko, IC I-524A, 10 μm, 10 cm × 4.6 mm i.d., 45 μequiv/mL, polymethacrylate base. [e] See ref (OVR, 1988). Shiseido, capsule pack, 3 mm, ODS, silica base, 3.5 cm × 4.6 mm i.d.

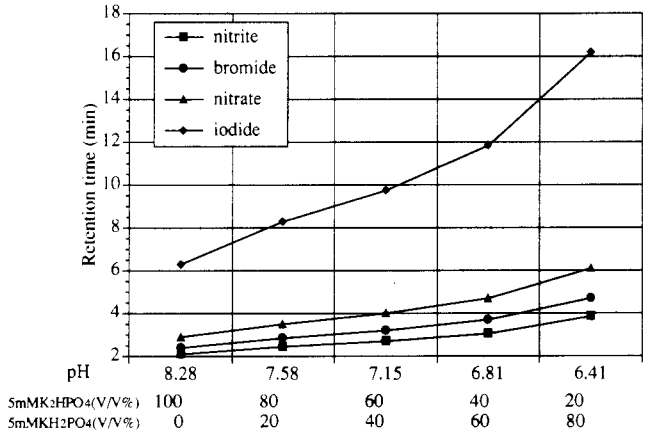

Figure 2. Effects of the mobile-phase pH on retention time. The components of the mobile phase were changed by blending 5 mM disodium phosphate and 5 mM sodium dihydrogen phosphate. The pH values of the mixture were measured by a pH meter. Fifty nanograms of standard was injected.

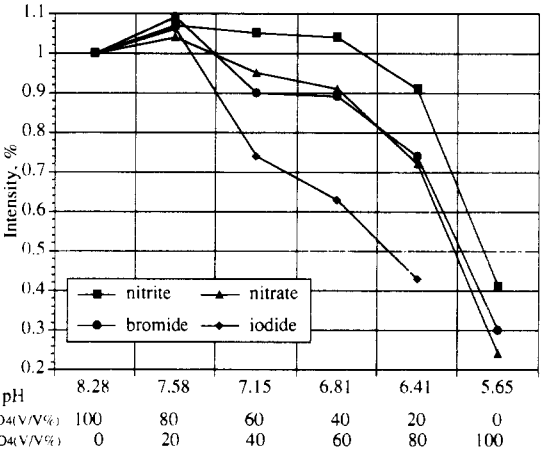

Figure 3. Effects of mobile-phase pH on peak intensity. See the legend to Figure 2.

to digest because of saponification and insufficient digestion. If interference cannot be removed, the sample should be ashed by means of the proposed procedure (Grave and Grevenstuk, 1979; OVR, 1988).

Basically, ashing is significant to convert several bromine oxides to bromide. However, bromine oxides may exist in several chemical forms without oxidation. Digestion with hydrogen peroxide and sodium hydroxide will convert bromate into bromide.

$$BrO_3^- + 3H_2O_2 \xrightarrow{OH^-} Br^- + 3O_2 + 3H_2O$$

Under our conditions, 47–70% of bromate was converted to bromide (Figure 4).

On the other hand, recovery after ashing in a muffle was examined by heating potassium bromide at 550 °C overnight. The recoveries of bromide were 112, 71, and 65% after 6, 20, and 28 h of ashing, respectively. However, food samples were not ashed at 6 h under our conditions; it usually requires 16–20 h. The bromide levels of the same samples used in the recovery test for microwave digestion were determined by a procedure involving ashing (Grave and Grevenstuk, 1979). The bromide levels for pork and tomato juice were 3.6 and 3.0 ppm, respectively. These values were comparable with those obtained by the microwave digestion.

Therefore, overall recovery of bromide after digestion was comparable to that obtained by ashing with the muffle furnace. These results show that the digestion involving

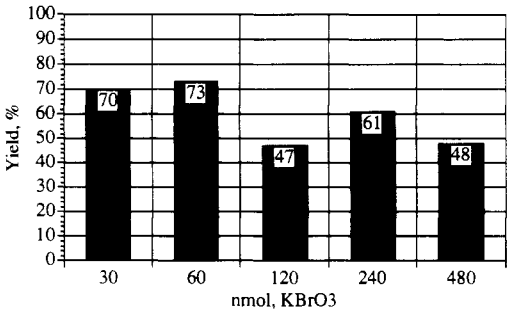

Figure 4. Conversion of potassium bromate into potassium bromide by digestion. Potassium bromate (30–480 ng) was heated with 10 mg of sodium hydroxide and 40 μL of 30% hydrogen peroxide at 200 W for 2 min. The samples were analyzed for bromide as described in the text.

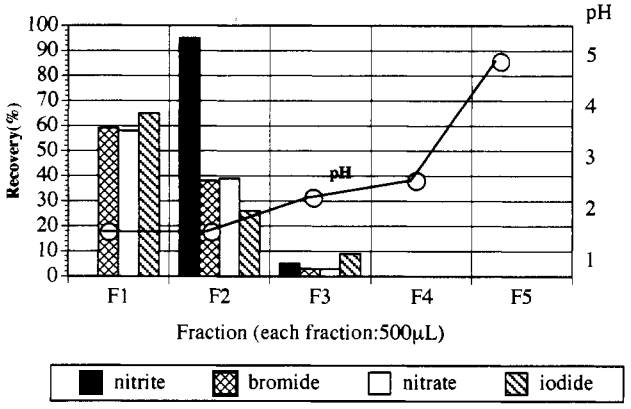

Figure 5. pH of sample fractions and elution profiles of anions from cation-exchange column. Resin (4 mL) was packed in a glass column (10-mm i.d.). The standard (500 ng) was dissolved in 500 μL of 0.5 N sodium hydroxide. (Open circle) pH value of each fraction.

hydrogen peroxide and sodium hydroxide is an adequate sample preparation for bromide determination.

Removal of Sodium Ions and Elution Profile of Bromide from a Cation Exchanger. After digestion or ashing, the sample contains a large amount of sodium hydroxide, which would interfere with the separation by ion chromatography. To remove the sodium ions in the sample and lower the pH of the solution, the digested sample was eluted through a cation-exchange resin. The sodium ions were substituted protons of cation-exchange resin and were trapped at the active sites of resin. As a result, the pH of the sample fractions was lowered from 2 to 5 (Figure 5, open circle indicates pH value of each fraction). Overwashing increases the pH value of the fraction.

The elution profiles of the ions from a column packed with 1 g of resin are shown in Figure 5. Nearly 95% of the added ions were recovered after two washes with 500 μL of water. This implies samples require at least three fractions to process all anions for analysis.

Recoveries apparently are not reduced, even when the sample contains a large amount of chloride. For example, with standard solutions involving 25 μg of bromide, nitrate, and iodide in 2% sodium chloride digested as described, recoveries for bromide, nitrate, and iodide were 105, 85, and 67%, respectively. The recovery of iodide was low because it was unstable under our conditions.

The effect of the sample pH on the retention time was examined by changing the pH with sulfuric acid because too much exchanging resulted in lower sample pH. Standard (500 ng) was dissolved in 500 μL of diluted sulfuric acid. The retention time was not affected.

Table 2. Recovery[a]

foodstuff	spiking level (μg/g)	recovery (%)	CV%
miso	25	109	12.3
	50	119	2.8
tomato juice	25	99	12.9
	50	91	5.8
pork	25	110	13.6
	50	108	7.2
bread	25	109	18.9
	50	87	2.6

[a] Background levels for each sample are 68 (miso soup), 55 (tomato juice), 17 (pork), and 38 (bread) ppm. The values were means of three determinations.

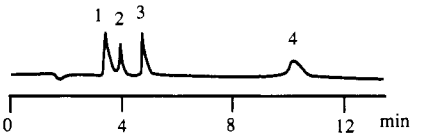

Figure 6. Chromatograms for standard solutions (3.3 μg/mL): (1) nitrite; (2) bromide; (3) nitrate; (4) iodide. Column used was Tosoh TSK gel IC-Anion-PWXL.

However, the shapes of the peaks for bromide and other ions were changed and were inadequate for analysis. Reverse peaks appeared near that of the bromide and interfered with the analysis in 0.1 N sulfuric acid.

In spite of these effects, sodium ion removal using a cation exchanger serves its purpose for bromide analysis.

Recovery Test. To evaluate the procedure for bromide determination, recovery tests were conducted by adding 2.5 and 5.0 μg of potassium bromide to 100-mg samples. The results are shown in Table 2, and corresponding chromatograms are shown in Figures 6 and 7. Thus, recoveries were sufficient for checking bromide levels in food. The CV% were relatively large, which resulted from sample inhomogeneity. The sample size for this procedure is 100 mg, which is limited by the capacity of the pressure vessel. A larger vessel would resolve this problem. Background levels for bromide were rather high in samples for recovery test, and we could not find low-level samples for spiking. The background levels were calculated by means of standard addition method (Day and Underwood, 1967; Japan Society for Analytical Chemistry, 1960). This procedure was developed to determine analyte at levels lower than the limit of quantitation of the analytical procedure and is applicable to the calculation.

Cautions for Analytical Procedure. Added hydrogen peroxide and sodium hydroxide for digestion also disturbed the analysis. Hydrogen peroxide absorbs UV in the same range as bromide. If a large amount of hydrogen peroxide remains, a bromide peak will appear on the tail of hydrogen peroxide. When sodium hydroxide remains in the sample solution, the retention times of analytes change and the bromide peak is overlapped. Chloride will not disturb the determination of bromide, because the monitor was operated at 205 nm at which chloride has no absorption. However, although these are potential problems, throughout the recovery tests, hydrogen peroxide, sodium hydroxide, pH, chloride, and others did not interfere with the analysis. Therefore, the overall procedure proposed is a suitable one for bromide analysis.

Analysis of Total Diet Study Samples. To determine the applicability of this procedure, several samples prepared for a total diet study were analyzed. After the food items were purchased at local grocery stores, those requiring cooking were prepared as if they were to be served and eaten at home. Each foodstuff was blended or chopped to homogeneous consistency and combined in an ap-

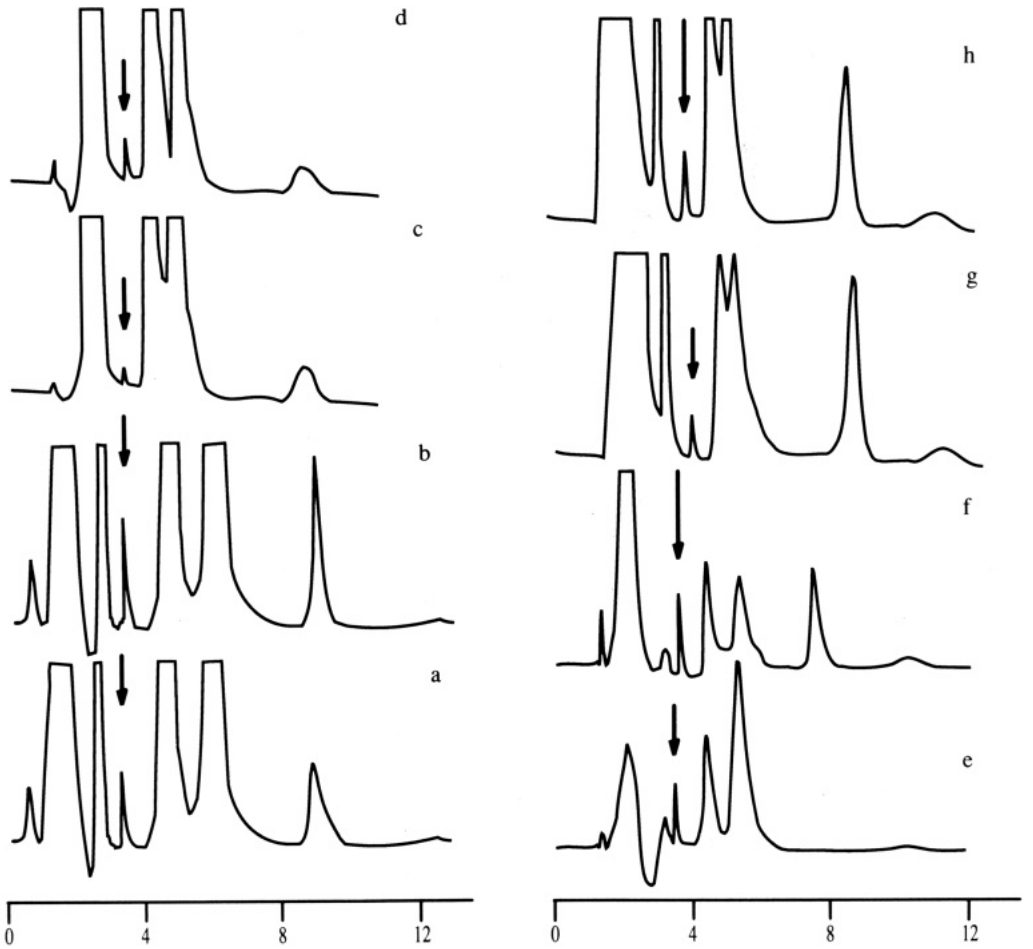

Figure 7. Chromatograms of control and spiked samples: controls of miso soup (a), pork (c), tomato juice (e), bread (g): spiked samples (2.5 μg/100 mg) of miso soup (b), pork (d), tomato juice (f), bread (h).

Table 3. Monitoring Results for Total Diet Study

	concn, ppm (CV%)	
group	1990	1991
1	10 (40)	14 (23)
2	21 (11)	N/A[a]
3	12 (17)	7 (17)
4	15 (32)	19 (18)
5	N/A	13 (32)
6	12 (22)	N/A
7	23 (18)	15 (40)
8	16 (9)	26 (3)
9	N/A	N/A
10	12 (27)	N/A
11	21 (3)	8 (23)
12	15 (25)	5 (23)
13	19 (7)	17 (3)

[a] N/A, samples were not available.

propriate proportion with similar items to form a specific composite. The diets reflect quantities consumed by adults as surveyed by the Japanese government in 1990 and 1991. The diet consisted of 111 foods divided into 13 food groups. These procedures meet the recommendation in "Guidelines for the study of dietary intakes of chemical contaminants" (FAO/WHO, 1983). Some of the food groups were no longer available because those samples were used for the original total diet study.

The results are shown in Table 3 and Figure 8. Comparable data are not available because bromide was not analyzed in the total diet study in Japan. However, the first total diet study conducted by the U.S. government involved bromide (FDA, 1963), and the values were comparable (Duggan et al., 1966).

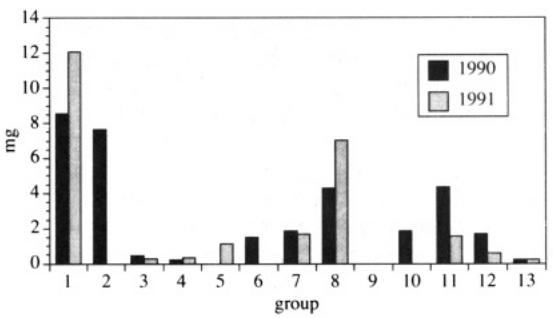

Figure 8. Daily intakes of bromide from food groups.

Food group IV was difficult to digest by our procedure, so the sample was ashed as reported (Grave and Greven-stuk, 1979). This sample contained fats and oils and saponified as digestion proceeded. Particles of saponified components separated from the mixture and floated onto the surface of the solution. The sample was inhomogeneous and was therefore ashed in the muffle.

From the results of Figure 8, estimated daily intakes of bromide from food were calculated and are 32.5 (1990) and 24.9 mg (1991). Those values are low and safe for adults (normal body weight is considered to be 50 kg). The acceptable daily intake for inorganic bromide is 1 mg/kg of body weight.

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