Multielement Analysis of Commercial Mineral Waters by Chelating Resin Preconcentration and ICP-MS

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Abstract Trace metals in commercially-available 18 mineral waters were determined by ICP-MS, where a chelating resin-packed minicolumn was applied to separate matrix elements as well as to preconcentrate trace metals in the samples. The 25-fold concentration for trace metals was obtained by preconcentrating 50 ml of mineral water to 2.0 ml of final analysis solution. At the same time, matrix elements were substantially eliminated, so that trace metals could be determined by ICP-MS on the multielement basis. The validation of the present analytical method was examined by determining trace metals in river water reference material (JAC 0032). In addition, trace metals in tap water from Nagoya city were determined by the present method, and their concentrations were compared to those in mineral water.

Key words: multielement analysis, mineral water, chelating resin-packed minicolumn, preconcentration, ICP-MS

Introduction

The consumption of mineral water is significantly increasing all over the world, which is seen from the fact that there are more than 2900 brands of mineral waters in 118 countries [1], and also from the fact that the annual per capita consumption in each of Italy, Mexico, Belgium, Germany, and France exceeded even 100 liter [2]. As a result, the analyses of the mineral contents, radioactivity, and organic compounds in mineral waters have been extensively performed to investigate their suitability as drinking water [3-11]. Taking into account the tremendous consumption of mineral waters, the researches on the compositions and constituents in mineral water should be carried out even from the analytical points of views. In addition, trace metals often provide great biomedical effects on human health, because it is known that Fe, Mn, Zn, Cu *etc.* are bio-essential, while Hg, Cd, Cr(VI) *etc.* are toxic [12, 13]. Therefore, it is desirable that the concentrations of trace metals in mineral waters, as one of the major sources for intake of such constituents, are examined in detail.

In general, inductively coupled plasma mass spectrometry (ICP-MS) provides excellent analytical features of multielement detection capability with high sensitivity and wide linear dynamic range, which allows the direct determination of trace metals in the wide concentration range even at sub-ppb ($\mu g\ l^{-1}$) level [12, 13]. However, the direct determination of trace metals in mineral waters by ICP-MS is still difficult, because their concentrations are extremely low, for example at ng l^{-1} level. Consequently, preconcentration of trace metals together with separation of matrix elements are necessary for the determination of them in mineral waters. In the present experiment, a chelating resin-packed minicolumn developed by the present authors [14] was applied to the pretreatment of mineral waters for the determination of trace metals, where commercially-available 18 mineral waters were investigated, along with the tap water from Nagoya city.

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Samples and method

Mineral water samples

Mineral waters bought from the markets in Nagoya city were investigated in the present experiment, along with the tap water from Nagoya city. Mineral waters used in the present work are summarized in Table 1, along with the information on their producing areas, and water hardness. All of these mineral waters were bottled in PET bottles

Table 1 List of mineral waters used in the present work

Brand name	Producing area	Hardness / μg l^{-1}
Vittel	France	307
Evian	France	291
Valvert	Italia	177
Masafi	U.A.E	85
Volvic	France	60
Ice filed	Canada	28
Umi-no-shinso-sui (Muroto)	Kochi, Japan	250
Ryusendo-no-mizu	Iwate, Japan	97
Rokko-no-oishii-mizu	Kobe, Japan	84
Fuji mineral-water	Yamanashi, Japan	74
Sikotu-no-hisui	Hokkaido, Japan	63
Yufuin / Wakasui	Oita, Japan	63
Vanadium water	Yamanashi, Japan	32
Suntory Natural-mineral-water	Yamanashi, Japan	30
Misumi-no-junsui	Shimane, Japan	24
Hisui / Nagara river	Gifu, Japan	18
Shimanto-no-gensui	Kochi, Japan	16
Jomonsui	Kagoshima, Japan	10
Nagoya city tap water	Nagoya, Japan	26

Table 2 Analytical results for trace elements in river water certified reference material (JAC 0032).

Element	*m/z*	Observed value [a] / μg l^{-1}			Certified value / μg l^{-1}		
Al	27	67	±	3	61	±	2
Ti	47	0.6	±	0.06			
V	51	7.9	±	0.3	8.2	±	0.3 [c]
Mn	55	4.8	±	0.5	5.4	±	0.1
Fe	57	74	±	3	57	±	2
Co	59	0.27	±	0.03			
Ni	60	10.7	±	0.9	10.2	±	0.3
Cu	65	9.8	±	0.8	10.5	±	0.2
Zn	66	10.2	±	0.9	11.3	±	0.4
Ga	71	0.017	±	0.003			
Y	89	0.0087	±	0.0004	0.0082	±	0.0003 [c]
Zr	90	0.0093	±	0.0009			
Mo	95	0.54	±	0.08	0.49	±	0.01 [c]
Sn	118	n.d. [b]					
W	184	0.028	±	0.004			
Pb	208	11	±	1	9.9	±	0.2
U	238	0.0025	±	0.0002	0.0026	±	0.0007 [c]

a) Mean value ± standard deviation, $n = 3$. b) Not detected.
c) Cited from Ref. 15.

with plastic caps. Before performing the preconcentration, they were acidified to pH 1 with *conc.* nitric acid. Besides, river water reference material (JAC 0032) issued from the Japan Society for Analytical Chemistry (JSAC) was also analyzed for evaluating the reliability of analytical method employed in the present experiment.

Analytical method

A chelating resin-packed minicolumn developed by the present authors [14] was applied to the pretreatment of mineral waters. The 25-fold preconcentration of trace metals in mineral waters was carried out in the present experiment, where 50 ml of mineral water sample was adjusted to pH 5.0 and loaded to the minicolumn. After rinsing the minicolumn with 5 ml of 1 M ammonium acetate buffer (pH 5.0) to minimize the amounts of matrix elements retained in the minicolumn, trace metals adsorbed on the resin were eluted with 1.8 ml of 2 M nitric acid solution, and 0.2 ml of internal standard solution (Ge, In, Re, and Tl 100 ppb each) was added in the above eluted solution to correct matrix effects. Thus, 2.0 ml of sample solution was finally obtained as the analysis solution, which was subjected to the determination of trace metals by ICP-MS (Agilent HP4500, Yokogawa, Tokyo, Japan).

Results and Discussion

Analytical results for trace metals in JAC 0032

In order to evaluate the reliability of the results obtained in the present experiment, trace metals in river water reference material (JAC 0032) were determined by the present method described in the experimental section. The results are summarized in Table 2, along with certified values or reference values reported by Itoh *et al.* [15]. It is seen that the results for the concentrations of Al, V, Mn, Ni, Cu, Zn, Y, Mo, Pb, and U agreed well with certified values or reference values, which indicated that the present method was suitable for the determination of trace metals in fresh water. The relatively larger concentration observed for Fe might be caused by the interference of $^{40}Ca^{16}O^{1}H$ with ^{57}Fe.

Analytical results for trace metals in mineral waters

The analytical results for trace metals in mineral waters are shown in Fig. 1 (a-d), along with those in Nagoya city tap water (sampled in Nagoya University) and the concentration criteria for tap water quality issued by the government of Japan. It is seen from Fig. 1 that trace metals in all mineral waters were less than the concentration criteria for tap water quality, which mean that these mineral water were safe for drinking, although no criteria for V, Zr, Sn, Ti, Y, Ga, and W were available. It should be noted here that bio-essential trace metals in most of mineral waters were less than those in tap water, while mineral waters from Europe generally contained high concentration of U compared with mineral waters from Japan and tap water, especially for Evian (France), the concentration of U was 100-fold higher than those in other mineral waters. Such large contents of European mineral waters may indicate that they are originated from the calcium carbonate layers. In addition, Vanadium water from Yamanashi contained V at *ca.* 100 μg l^{-1}, which was much higher than those in other mineral waters. It is conclusively noted here that, in addition to trace metals examined here, other parameters such as content of organic matter and fluoride in mineral waters should be investigated to evaluate in detail the water qualities of mineral waters as drinking water.

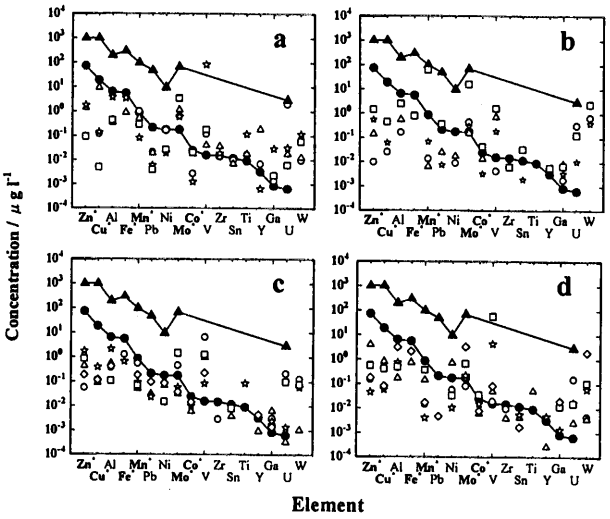

Fig. 1 Comparison of the concentrations for trace metals in commercial mineral waters and Nagoya city tap water, Bio-essential elements are shown in bold fonts with *.

a ○:Evian, △: Umi-no-shinso-sui (from Muroto), □: Rokko-no-oishii-mizu, ☆: Vanadium Water; Nagoya city tap water, ▲: Tap water quality criteria, Japan

b ○: Vittel, △: Ryusendo-no-mizu, □: Yufuin / Wakasui, ☆: Hisui / Nagara river, ●: Nagoya city tap water, ▲: Tap water quality criteria, Japan

c ○: Volvic, △: Ice field, □: Suntory Natural-Mineral -Water, ☆: Shimanto-no-Gensui, ◇: Jomonsui, ●: Nagoya city tap water, ▲: Tap water quality criteria, Japan

d ○: Valvert, △: Masafi, □: Fuji mineral water, ☆: Sikotsu-no-hisui, ◇: Misumi-no-junsui, ●: Nagoya city tap water, ▲: Tap water quality criteria, Japan.

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