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Multielement Neutron Activation Analysis of Underground Water Samples

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An instrumental neutron activation analysis by gamma-ray spectrometry with high resolution and large volume Ge (Li) detectors followed by data processing with an electronic computer was applied to the multielemental analysis to elucidate the chemical qualities of the underground water which has been widely used in the *sake* brewing industries in Mikage, Uozaki and Nishinomiya districts, called as *miyamizu*. The evaporated residues of the water samples were subjected to the neutron irradiations in reactor for 1 min at a thermal flux of $1.5 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ and for 30 hrs at a thermal flux of $9.3 \times 10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ or for 5 hrs at a thermal flux of $3.9 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. Thus, 11 elements in the former short irradiation and 38 elements in the latter two kinds of long irradiation can be analyzed. Conventional chemical analysis including atomic absorption method and others are also applied on the same samples, and putting the all results together, some considerations concerning the geochemical meaning of the analytical values are made.

KEY WORDS: Neutron activation analysis / Chemical analysis /
Multielement analysis / Lyophilization / Correlation coefficient /
Dissolving origin / Water quality /

I. INTRODUCTION

Recent advances in instrumental neutron activation analysis make multielemental analysis possible for various kinds of samples. This paper describes the application to underground water samples. The wells under our investigations are situated on the alluvial plain in the southern parts of Mt. Rokko range, which are composed mainly of biotite granite and partly of granodiorite and thin Paleozoic Strata. And, since 1840, some of them in the Nishinomiya district have been used as the source of the most suitable water for the *sake* brewing process, called as *miyamizu*.

In our activation analysis reported here, a short and a long irradiation methods are applied and total 46 elements can then be analyzed, and 20 chemical components are also simultaneously determined by conventional chemical analysis and, putting all the results

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obtained together, some geochemical meanings concerning the origins of the dissolving species are considered here.

II. EXPERIMENTAL

1. Samples

The underground water samples to be studied were taken by an acrylic resin-made water sampler (inner volume : about 3 l) at the wells to be investigated, the addresses of which are given in Table I. The waters are welling out of the relatively shallow layers of less than 10 m from the ground surface. The sampling dates were October 6th and 7th of 1978 for the A series samples, and July 3rd, 11th and 23th of 1979 for the B series samples.

Table I. Sampling Location

Sample No.	Location	Division
A 1, B 1	Mikagehonmachi 2 chōme, Higashinada-ku, Kobe	} Mikage
A 2, B 2	Mikagehonmachi 5 chōme, Higashinada-ku, Kobe	
A 3, B 3	Mikagehonmachi 2 chōme, Higashinada-ku, Kobe	
A 4, B 4	Sumiyoshihonmachi 4 chōme, Higashinada-ku, Kobe	
A 5, B 5	Mikagehonmachi 2 chōme, Higashinada-ku, Kobe	
A 6, B 6	Uozakinishimachi 1 chōme, Higashinada-ku, Kobe	} Uozaki
A 7, B 7	Uozakinishimachi 1 chōme, Higashinada-ku, Kobe	
A 8, B 8	Uozakiminamimachi 4 chōme, Higashinada-ku, Kobe	
A 9, B 9	Uozakiminamimachi 4 chōme, Higashinada-ku, Kobe	
A10, B10	Uozakiminamimachi 5 chōme, Higashinada-ku, Kobe	
A11, B11	Kubochō, Nishinomiya	} Nishinomiya
A12	Hamachō, Nishinomiya	
A13	Sekizaichō, Nishinomiya	
B12	Sekizaichō, Nishinomiya	
A14	Kubochō, Nishinomiya	
A15, B13	Kubochō, Nishinomiya	
A16, B14	Kubochō, Nishinomiya	
B15	Kubochō, Nishinomiya	
B16	Kubochō, Nishinomiya	
A17, B17	Yōgaicho, Nishinomiya	
A18, B18	Sumiyoshi River	} R. Sumiyoshi
A19, B19	Sumiyoshi River	
A20, B20	Sumiyoshi River	

In the samples to be studied, Sumiyoshi River was also included, because this stream is assumed to represent a typical fresh water in the Rokko range as far as the bulk element composition is concerned.¹⁻³⁾

The waters to be analyzed were filtered through Millipore filters with the pore size of 0.45 μm (HAWP 04700), which were already washed with the immersion in hot 2 N HNO₃ for 2 hrs and then in pure water.

Every 300 ml aliquots of the sample waters were transferred to a 500 ml-Teflon bottle

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and then frozen at -70°C . The frozen samples were placed in the freeze-drying chambers which then were evacuated. Two or three days under a vacuum of 10^{-4}mm Hg was needed to dry a 300 g of ice to a residue, which remains on the bottom of the bottle.

Since the freeze-drying process is essentially a low temperature and a low pressure distillation in an air-tight system, the preconcentration process virtually eliminates sample contamination and volatile element loss. However, a question may be raised regarding the ability to transfer the dry residue quantitatively from the freeze-drying container to an irradiation container.⁴⁾

The residues in our studies were transferred quantitatively to clean 100 ml-Teflon beakers with the aid of small amounts of a mixture of ethanol and water (1: 2) and then dried overnight in an air bath of 120°C under a clean condition. The each residue obtained was then transferred to two clean polyethylene irradiation bags, one of which was used for the short irradiation and the others for the long irradiation. The estimated recoveries in transferring to the irradiation bags were in 70 to 90 % and the weights of the residue to be irradiated were 20 to 50 mg.

Before the experiments, all the above plastic apparatus were soaked in 4 N HNO_3 for 24 hours to remove surface contamination and dried after water washings.

The bags used to contain the sample residues were made by 0.0035 cm thick linear polyethylene film. The film was cut and heat-sealed to make 1.5 cm square form. The weight to be irradiated and then measured together with the sample residues was in 20 to 30 mg. Typical trace element concentrations in the acid-washed bags and the results of this blank contribution study are given in Table II.

Table II. Trace Element Content of Polyethylene Film Used as Sample Bags

Element	Concentration (ppm)	Necessary correction ($\mu\text{g/l}$)
Na	38.1	6.1 ~ 13.6
Mg	27.6	4.4 ~ 9.9
Al	5.11	0.82 ~ 1.83
Cl	120	20 ~ 44
Ca	16	2.6 ~ 5.7
Ti	3.3	0.53 ~ 1.16
V	0.012	0.0020 ~ 0.0044
Mn	0.14	0.022 ~ 0.049
Cu	1.3	0.20 ~ 0.45
I	0.20	0.033 ~ 0.072

The standard samples used for the analysis were prepared from analytical grade reagents. Dependings on half-life and gamma-ray energies of the nuclides produced and the chemical properties of the elements in question, the standards were mixed together into an appropriate number of multistandard specimens.⁵⁾ The multistandard specimens were neutron-irradiated and gamma-ray measured in the similar method with the sample to be analyzed.

2. Neutron irradiation and radioactivity measurement

Neutron irradiation in the short life method were carried out for 1 min using the pneumatic tube system in a TRIGA Mark II Reactor of Musashi Institute of Technology with a thermal neutron flux of $1.5 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. After 3.0 min from the end of irradiation, radioactivity measurement by the GAMA system⁶⁻⁸⁾ with a 77 cc coaxial Ge (Li) detector (Canberra Model 7229, FWHM 1.98 keV at 1.33 MeV), at a fixed position of 7.0 cm distance from the detector surface, and using an on-line computer data analyzer, was carried out for 300 sec. The elements determined by this method, the corresponding radionuclides and the gamma-ray energies used in the measurements are given in Table III.

Table III. Elements Determined by I. N. A. A. of Underground Water Samples (short life method)
1 min irr. -3 min cooling -300 sec counting

Element	Nuclide	Half-life	Gamma-ray energy (kev)
Na	²⁴ Na	15.02h	1369
Mg	²⁷ Mg	9.46m	844
Al	²⁸ Al	2.25m	1779
Cl	³⁸ Cl	37.2 m	2168
Ca	⁴⁹ Ca	8.72m	3084
Ti	⁵¹ Ti	5.76m	320
V	⁵² V	3.76m	1434
Mn	⁵⁶ Mn	2.58h	847
Cu	⁶⁶ Cu	5.10m	1039
Br	⁸⁰ Br	17.4 m	616
I	¹²⁸ I	25.0 m	443

Table IV. Elements Determined by I. N. A. A. of Underground Water Samples (middle life method)
30 hr irr. -1 week cooling -4~6×10³ sec counting

Element	Nuclide	Half-life	Gamma-ray energy (kev)
Na	²⁴ Na	15.02h	1369
K	⁴² K	12.36h	1525
Ga	⁷² Ga	14.1 h	834
As	⁷⁶ As	26.3 h	559
Br	⁸² Br	35.4 h	777
Mo	⁹⁹ Mo	66.02h	181
	^{99m} Tc	6.02h	141
Cd	¹¹⁵ Cd	53.5 h	528
	^{115m} In	4.5 h	336
La	¹⁴⁰ La	40.2 h	1596
Sm	¹⁵³ Sm	46.5 h	103
Gd	¹⁵⁹ Gd	18.6 h	364
W	¹⁸⁷ W	23.9 h	686
U	²³⁹ U	23.5m	
	²³⁹ Np	2.35d	278

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Table V. Elements Determined by I. N. A. A. of Underground Water Samples (long life method)
30 h irr. -2~3 week cooling -4×10⁴ sec counting

Element	Nuclide	Half-life	Gamma-ray energy (keV)	Element	Nuclide	Half-life	Gamma-ray energy (keV)
Ca	⁴⁷ Ca	4.54d		Sb	¹²² Sb	2.72d	564
	⁴⁷ Sc	3.41d	159		¹²⁴ Sb	60.3 d	1691
Sc	⁴⁶ Sc	83.8 d	889	Cs	¹³⁴ Cs	2.06y	796
Cr	⁵¹ Cr	27.7 d	320	Ba	¹³¹ Ba	11.7 d	496
Fe	⁵⁹ Fe	44.6 d	1099	Ce	¹⁴¹ Ce	32.5 d	146
Co	⁶⁰ Co	5.27y	1333	Nd	¹⁴⁷ Nd	11.0 d	531
Ni	⁵⁸ Co	70.8 d	811	Eu	¹⁵² Eu	12.4 y	1408
Zn	⁶⁵ Zn	243.7 d	1116	Gd	¹⁵³ Gd	241.5 d	103
Se	⁷⁵ Se	120 d	265	Tb	¹⁶⁰ Tb	72.3 d	299
Rb	⁸⁶ Rb	18.7 d	1077	Yb	¹⁶⁹ Yb	31 d	198
Sr	⁸⁵ Sr	64.9 d	514		¹⁷⁵ Yb	4.19d	396
Ag	^{110m} Ag	250.4 d	658	Lu	¹⁷⁷ Lu	6.71d	208
Sn	¹¹³ Sn	115.1 d		Hf	¹⁸¹ Hf	42.4 d	482
	^{113m} In	1.65h	392	Ta	¹⁸² Ta	115 d	1221
	^{117m} Sn	14 d	158	Hg	²⁰³ Hg	46.6 d	279
				Th	²³³ Th	22.2 m	
					²³³ Pa	27 d	312

Neutron irradiation in the long life method were carried out in a swimming pool reactor of Kyoto University, for 30 hrs using the graphite thermal column irradiation system (thermal neutron flux of $9.3 \times 10^{10} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$), or for 5 hrs using the slant irradiation hole system (thermal neutron flux of $3.9 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$) in which case the sample was sealed in a quartz tube (7 mm i. d., 40 mm l., 0.5 mm thickness) and, after the irradiation, leached out with 5 ml of 2 N HNO₃. After 1 week from the end of irradiation, the first gamma-ray spectrometry using a 50 cc coaxial Ge(Li) detector and computer system of Radiation Center of Osaka Prefecture⁹⁾ was carried out for 4×10^3 or 6×10^3 sec and, then after the 1 to 2 weeks decay, the second gamma-ray spectrometry using the same system was made for 4×10^4 sec. The elements determined by these methods are given in Tables IV and V.

3. Chemical analysis

Parallel to the present work, in order to get as many informations on the water qualities as possible, the water samples taken simultaneously with those investigated in this work were analyzed with the following conventional analytical methods. The atomic absorption methods for Ca, Mg, Fe, Mn, Cu and Zn, the flame photometric methods for Na and K, the absorption spectrochemical methods for Cl, SO₄, SiO₂, PO₄, BO₃ and V, and the titrimetric methods for HCO₃ and COD were applied. And the APDC chelate components of Fe, Mn, Cu and Zn¹⁰⁾, which are formed at pH 5.5 in the sample aqueous phases and extracted into CHCl₃, were also determined by the atomic absorption methods.

III. RESULTS AND DISCUSSION

1. Chemical analysis

The results of the chemical analysis performed on the A series samples taken in 1978 and on the B series samples taken in 1979 are presented in Tables VI and VII, respectively.

The elements marked with asterisk in the tables are the species extracted as the APDC chelates.

2. Neutron activation analysis

The results in 1978 and 1979 are presented in Tables VIII and IX, respectively.

Although the neutron activation values of Na, Cl, Ca, K, Mn and Cu did not show any bias with respect to the conventional analytical methods, these values are excluded from these tables, because it is considered that the values by the conventional analysis given in Tables VI and VII are more precise.

The blank values attributed to the impurities in the polyethylene bags used as the envelope of the sample residues were negligible, because these values, as shown in Table II, were less than 5.0 % of the values for each elements determined in the samples.

Thus, it could be concluded that the values of Al, V, I, As, Br, Sc, Cr, Co, Se, Ba, Rb, Sr, Sb and Cs in the tables are applicable in making the geochemical considerations concerning the water qualities of these objects.

3. Water qualities in each district

The arithmetic means and standard deviations of the analytical values obtained in 1978 and 1979 (Tables VI~IX), classified to Mikage, Uozaki, Nishinomiya and R. Sumiyoshi, are given in Table X.

3.1 Major components

The sums of Ca, Mg, Na, K, HCO_3 , Cl, SO_4 and SiO_2 values in the each districts exceeded 95 % of the values of the evaporated residues, as shown in Table X. These components, therefore, can be regarded as the major dissolved components*. Considering on these components, the following conclusions could be made.

(i) The Uozaki are approximately 1.8 times of the R. Sumiyoshi, except the SiO_2 , and, but, are less than the Mikage and the Nishinomiya. This is shown that the influence of river for the underground water is more powerful in Uozaki than in Mikage and Nishinomiya.

(ii) The Mikage are approximately two times of the Uozaki.

(iii) The Nishinomiya are approximately 1.2 times of the Mikage, except the SO_4 constancy.

(iv) Generally speaking, in the compositions of the main dissolved components, that is in the relative contents, there is a close similarity between the three districts. This

* In the later additional experiments, it was shown that, if the NO_3 values are added to these sums, approximately 100% values can be obtained.

Table VI. Results of Chemical Analysis in 1978 Samples

No.	pH	ppm										ppb								
		E.R.	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	SiO ₂	PO ₄	BO ₃ -B	Fe	Fe*	Mn	Mn*	Cu	Cu*	Zn	Zn*
A-1	6.4	315	43.1	6.51	23.8	3.8	91.1	26.0	49.8	18.3	0.036	58.2	18.5	3.6	1.9	1.1	4.1	4.8	13.4	11.6
A-2	7.3	246	27.9	3.06	18.6	9.5	64.7	23.0	33.0	17.5	1.93	30.6	—	2.6	—	0.7	—	2.6	—	3.8
A-3	7.1	333	44.8	6.65	23.8	5.9	100.8	24.5	52.5	20.8	0.082	53.4	15.3	1.8	1.8	1.8	3.7	1.1	12.5	8.0
A-4	7.0	254	39.3	4.85	16.0	4.2	93.4	18.0	37.5	14.0	0.534	42.0	11.7	2.3	10.0	0.4	2.8	2.3	6.7	3.4
A-5	7.1	271	28.3	6.23	23.8	5.6	96.8	32.5	14.0	30.8	0.226	37.8	14.0	4.9	2.3	2.0	2.6	1.6	9.5	3.6
A-6	6.8	165	27.9	3.06	8.7	2.3	65.9	7.0	18.8	12.8	0.064	20.6	11.7	3.6	1.1	0.9	7.8	6.5	8.9	6.2
A-7	7.0	150	19.0	1.82	7.7	1.7	58.4	5.0	10.6	15.5	0.023	18.2	15.6	1.6	0.7	0.6	0.6	0.9	4.5	2.6
A-8	6.8	166	21.5	3.06	17.2	5.0	71.6	13.0	18.5	14.0	0.095	25.6	14.3	2.0	1.3	0.5	0.4	1.8	7.4	5.4
A-9	7.1	140	21.5	3.20	8.9	2.7	57.3	8.5	16.6	13.5	0.238	19.6	13.6	1.6	1.3	0.6	0.2	0.3	4.9	2.1
A-10	6.9	156	23.2	2.51	7.7	2.7	62.4	6.5	15.1	12.8	0.025	19.4	11.7	1.6	1.4	0.5	1.9	0.4	8.6	3.5
A-11	7.2	328	41.9	8.16	34.6	9.8	95.1	68.0	37.3	17.5	2.24	62.4	15.6	4.4	1.6	1.3	1.9	1.5	9.5	4.7
A-12	7.2	348	51.6	12.16	20.2	10.5	129.5	30.0	41.9	20.8	2.25	72.6	11.0	3.8	16.6	65.2	2.8	4.5	9.3	4.3
A-13	7.4	350	58.4	5.96	20.6	10.0	139.2	25.0	37.5	27.0	5.36	106.6	83.4	12.6	1.8	0.6	15.7	14.9	34.9	29.2
A-14	7.4	300	43.6	8.44	22.0	8.4	93.4	30.5	45.5	23.0	4.69	79.0	22.4	8.0	2.5	1.4	4.3	4.5	137.6	110.9
A-15	7.1	267	35.9	4.71	21.4	6.8	74.5	19.5	37.6	24.3	7.56	—	12.7	2.7	1.1	0.9	3.0	1.3	10.1	5.5
A-16	7.1	331	49.9	9.54	22.5	12.9	122.0	21.5	48.5	26.5	8.18	—	19.5	2.2	1.6	0.7	3.2	1.6	15.4	4.7
A-17	7.0	255	33.0	6.23	24.5	8.5	79.6	26.5	39.5	19.0	4.36	40.0	—	2.8	—	1.8	—	1.7	—	4.1
A-18	7.4	58	16.6	1.68	8.0	1.2	48.7	5.7	8.5	13.5	0.023	18.6	—	5.0	—	0.9	—	1.1	—	2.6
A-19	7.4	93	13.9	1.54	7.0	1.0	40.7	4.4	13.0	13.8	0.013	8.8	12.1	11.5	2.8	4.2	1.3	0.8	4.4	2.3
A-20	7.4	117	24.1	2.09	8.2	1.0	72.2	4.6	9.0	13.4	N. D.	7.2	39.2	39.5	7.7	27.9	1.5	0.5	5.1	2.0

Table VII. Results of Chemical Analysis in 1979 Samples

No.	pH	E. R.	ppm										ppb								
			Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	SiO ₂	PO ₄	COD	V	Fe	Fe*	Mn	Mn*	Cu	Cu*	Zn	Zn*
B-1	6.5	300	50.9	6.12	23.5	5.0	96.7	25.6	48.4	24.9	0.16	0.70	0.52	22.0	4.3	3.1	1.0	1.4	1.9	10.8	8.1
B-2	6.5	270	35.5	6.12	36.9	12.8	91.5	51.4	42.5	24.4	1.79	0.73	0.96	15.6	3.6	3.4	2.0	5.4	2.5	8.0	4.6
B-3	6.5	317	55.9	6.96	25.4	5.1	97.3	29.8	53.1	26.0	1.60	0.21	0.58	10.6	1.8	1.9	0.9	3.4	2.4	8.3	8.2
B-4	6.8	197	37.8	3.88	18.9	6.8	106.0	16.6	21.6	20.5	0.73	0.67	0.86	14.9	2.0	1.5	0.8	4.6	1.5	5.9	4.5
B-5	6.7	310	56.4	6.92	24.2	9.1	122.2	33.6	44.2	25.9	0.74	0.40	0.22	10.6	3.6	549.7	499.2	5.0	2.2	4.6	3.5
B-6	6.8	189	56.3	7.00	14.2	3.5	68.3	10.8	30.1	16.2	1.51	0.27	0.22	8.5	1.9	1.6	0.4	5.8	3.7	12.3	10.8
B-7	7.0	105	38.3	3.64	8.9	1.3	62.0	7.0	1.0	15.0	0.03	0.06	0.12	7.7	1.1	1.1	0.4	3.4	1.9	5.6	3.0
B-8	6.8	185	28.6	4.20	15.0	3.2	66.6	22.6	18.7	15.3	0.19	0.15	0.18	6.3	1.8	0.9	0.5	1.8	0.5	2.8	3.3
B-9	6.9	136	22.3	3.16	10.6	2.1	59.1	9.9	14.9	16.2	0.25	0.27	0.22	4.9	1.7	1.0	0.4	1.0	0.4	4.6	2.8
B-10	7.0	183	36.1	2.92	10.1	3.9	71.8	11.8	26.8	17.6	0.26	0.34	0.10	9.9	2.3	1.1	0.5	1.8	0.5	4.6	2.1
B-11	7.0	221	27.9	4.57	30.1	6.6	58.5	42.6	30.0	19.7	2.35	1.34	1.06	17.3	6.8	6.4	6.4	2.4	2.3	6.5	4.9
B-12	7.0	347	70.4	5.81	28.0	10.2	141.3	36.0	41.9	27.2	3.25	2.04	1.11	93.0	50.2	3.0	1.8	8.2	5.5	13.1	12.8
B-13	7.1	317	50.2	7.90	39.5	10.0	89.8	56.8	35.2	28.8	3.80	1.05	1.66	13.2	7.8	1.7	0.5	6.2	5.9	41.2	30.0
B-14	7.1	321	62.7	7.67	23.5	11.8	124.5	35.0	34.3	34.0	5.70	1.59	1.62	24.3	6.5	2.3	0.6	4.5	3.0	7.9	7.9
B-15	6.9	354	73.1	8.86	25.6	12.2	137.8	41.6	47.5	30.1	5.45	1.46	1.80	16.6	7.1	2.3	0.6	9.9	8.3	9.4	6.8
B-16	7.0	265	55.6	5.47	17.0	10.0	119.3	23.0	29.9	33.0	5.88	1.34	1.62	40.2	9.0	1.6	0.3	17.3	15.2	18.1	19.3
B-17	7.0	296	54.2	7.28	26.1	10.0	120.4	30.4	36.2	25.1	3.10	1.18	1.06	14.6	7.5	249.7	248.1	3.8	3.0	7.9	9.7
B-18	7.4	87	16.1	1.23	8.8	1.9	38.8	6.7	10.7	20.3	<0.01	0.45	0.15	10.0	2.4	1.3	1.5	1.3	0.7	2.8	2.8
B-19	7.4	70	12.9	1.19	7.5	1.9	33.6	4.3	0.7	18.2	<0.01	0.63	0.26	7.9	3.0	0.8	1.0	1.6	0.7	3.2	2.5
B-20	7.3	103	24.0	1.87	8.7	2.1	59.6	6.6	12.6	19.7	<0.01	0.51	0.17	24.0	7.9	86.9	17.1	3.7	0.7	6.9	2.8

Table VIII. Results of Activation Analysis in 1978 Samples

No.	Al ppm	Ti ppb→	V	I	Ga	As	Br	Mo	Cd	La ($\times 10^{-1}$)	Sm ($\times 10^{-2}$)	Gd	W	U	Sc ($\times 10^{-2}$)	Cr	Co
A-1	0.18	<32	0.63	7.2	<14	0.58	67	<1	3	3.4	5.3	6.6	<1.0	<0.50	1.6	0.5	0.20
A-2	0.19	<49	1.8	25	<15	3.9	73	2	5	6.7	<1.3	<1.4	7	<0.88	0.3	0.45	0.097
A-3	0.15	<33	0.33	12	<14	0.70	69	1	2	3.4	0.7	0.6	<0.96	<0.44	1.2	0.20	0.072
A-4	0.12	<51	1.2	14	<13	2.2	51	1	4	2	<1.0	<0.82	<0.85	<0.67	0.71	<0.13	0.084
A-5	0.22	<27	0.57	13	<22	1.8	105	1	4	<0.76	<1.1	<0.68	<1.4	<0.67	0.55	0.59	—
A-6	0.13	<17	0.33	3.3	<13	0.65	32	3	4	<0.64	2	20	<0.81	0.8	0.1	0.75	0.34
A-7	0.11	<15	0.075	6.3	<11	0.54	21	4	7	1	1	1	<0.67	0.5	0.1	0.25	0.54
A-8	0.13	<33	0.50	6.6	<21	0.39	35	1	5	<1.2	<1.3	<0.6	<1.3	1	0.2	0.1	0.056
A-9	0.10	<28	0.28	5.2	<14	0.56	22	2	5	<1.0	<0.88	<0.46	<0.84	<0.78	0.15	<0.046	0.057
A-10	0.13	<31	0.16	7.8	<17	—	26	4	7	2	1.3	12	1	2	0.63	0.27	0.068
A-11	0.11	<98	0.79	19	<23	2.7	71	5	12	2	<1.3	<0.71	<1.3	5	0.31	0.46	0.094
A-12	0.13	<35	0.35	10	<18	2.4	52	3	25	<1.4	<1.0	<0.70	<0.95	5	—	<0.13	0.12
A-13	0.16	<70	1.5	30	<21	4.6	163	2	13	7.2	<1.2	<1.1	—	<1.5	—	2	1.1
A-14	0.12	<60	1.5	24	<21	2.1	74	2	7	4.5	<1.1	<0.90	<1.1	<1.3	1.7	0.4	0.42
A-15	0.14	<27	1.6	16	<21	4.0	48	2	2	<1.5	<1.1	<1.1	<1.1	<1.3	0.2	0.2	0.087
A-16	0.16	<33	2.3	32	<25	4.2	74	3	9	<1.6	<1.2	<1.2	<1.2	9	0.74	0.3	0.10
A-17	0.11	<26	1.1	17	<27	1.4	62	6	8	<1.7	<1.2	<0.97	<1.3	13	0.96	0.49	0.14
A-18	0.10	<4	0.12	1.8	<4	0.88	3.8	<1	2	8	1.3	2.6	<0.33	0.5	0.96	3.8	0.050
A-19	0.15	<7	0.32	4.7	<10	0.87	10	1	3	2	<1.0	<1.6	<0.76	0.9	2.1	0.1	0.047
A-20	0.11	<23	0.11	2.3	<6	0.50	11	3	1	0.9	2	20	<0.50	0.7	6	0.2	0.059

Table VIII. (continued)

No.	Se ppb→	Rb	Ag	Sb	Cs	Ba	Ce	Nd	Eu ($\times 10^{-2}$)	Gd	Yb ($\times 10^{-2}$)	Lu ($\times 10^{-3}$)	Hf ($\times 10^{-3}$)	Ta	Hg	Th
A-1	1.0	<1.1	<0.25	0.62	<0.053	10	<0.11	<1.4	<1.6	—	—	—	<3	<0.10	<0.1	<0.025
A-2	<0.63	11	—	0.55	<0.062	23	<0.17	<2.2	<1.5	<1.4	<2.6	<7.2	<4	<0.10	<0.2	—
A-3	<0.27	1.6	<0.18	0.20	<0.036	98	<0.078	<1.1	<0.99	0.6	2	6.8	<2	<0.08	<0.08	<0.018
A-4	<0.37	2.8	<0.22	1.5	—	80	<0.1	<1.4	<1.1	<0.82	<3.4	6.5	<2	<0.08	0.1	<0.025
A-5	<0.32	2.0	<0.20	0.53	0.05	50	<0.089	<1.3	<1.0	<0.68	<1.7	4	<2	<0.08	0.18	<0.021
A-6	0.2	<0.57	—	0.12	<0.023	27	<0.064	<0.74	<0.66	—	9	2.7	<10	<0.04	0.15	<0.013
A-7	0.3	<0.42	<0.09	0.12	0.02	18	<0.053	<0.54	<0.54	1	1	1	<10	<0.04	<0.08	<0.01
A-8	<0.26	<0.58	<0.15	0.29	0.04	39	<0.084	<0.92	<0.88	<0.6	<1.5	<1.8	<20	<0.06	0.22	<0.017
A-9	0.2	0.4	<0.11	0.15	<0.019	33	<0.064	<0.78	<0.53	<0.46	<1.4	<1.5	<10	<0.04	0.1	<0.014
A-10	0.29	0.6	<0.12	0.14	<0.022	<19	<0.073	<0.79	1	—	3	—	<10	<0.05	0.17	<0.014
A-11	<0.30	17	<0.17	0.49	<0.029	<24	<0.094	<1.4	0.7	<0.71	6.6	8.7	<20	<0.03	0.2	<0.022
A-12	1.1	14	<0.16	0.22	<0.026	<16	<0.096	<1.5	<0.43	<0.70	<0.37	7	<20	<0.03	0.26	<0.023
A-13	0.9	20	<0.26	1.4	<0.043	<21	<0.44	<2.0	<0.69	<1.1	—	—	<30	<0.05	<0.15	<0.035
A-14	1.0	15	<0.22	1.3	0.04	<19	<0.12	<1.8	0.8	<0.90	—	—	<30	—	<0.12	<0.03
A-15	0.8	10	<0.28	1.4	<0.043	<27	<0.15	<2.7	<5.4	<1.1	<6.5	<5.3	<30	<0.03	<0.15	<0.038
A-16	<0.55	25	<0.29	0.84	0.05	<30	<0.17	<2.9	<0.50	<1.2	<8.2	<6.2	<40	<0.03	<0.16	<0.042
A-17	<0.44	10	<0.22	1.2	<0.034	43	<0.14	<2.3	<0.62	<0.97	7	17	<30	<0.04	0.3	<0.034
A-18	3.5	<1.0	<0.30	0.028	<0.056	<14	<0.15	—	—	2.6	<1.3	3	—	0.10	<0.24	<0.029
A-19	<0.71	1.4	<0.45	0.28	<0.082	<21	<0.21	<2.0	—	<1.6	<2.0	<3.3	<40	<0.19	0.2	<0.042
A-20	<0.23	—	<0.15	0.065	0.05	42	<0.15	<0.78	<1.0	—	<0.77	2	<20	<0.08	0.25	<0.015

Table IX. Results of Activation Analysis in 1979 Samples

No.	Al ppm	Ti ppb→	I	As	Br	Gd	Sc ($\times 10^{-2}$)	Cr	Co	Se	Rb	Ag	Sb	Cs ($\times 10^{-3}$)
B- 1	0.14	<79	6.0	<0.74	70	<0.13	1.2	2.0	0.099	0.37	1.3	0.19	0.33	8.9
B- 2	0.13	<106	7.4	1.7	122	0.20	0.39	1.1	0.10	0.16	7.8	0.04	0.46	7.8
B- 3	0.12	<74	2.9	<1.1	86	<0.20	1.2	1.4	0.084	0.49	1.4	0.18	0.20	7.1
B- 4	0.13	<63	2.6	2.3	34	<0.16	0.27	0.87	0.065	0.15	1.9	0.11	1.2	2.4
B- 5	0.11	103	<3.3	5.1	106	<0.17	1.3	2.0	0.22	0.24	2.5	0.38	2.1	2.6
B- 6	0.09	<58	2.0	<0.77	34	<0.15	0.17	3.2	0.065	0.28	1.3	0.11	0.25	2.3
B- 7	0.08	<26	1.7	<0.92	52	<0.12	0.25	3.2	0.074	0.03	0.2	<0.013	0.36	2.1
B- 8	0.09	<47	2.9	<0.44	70	<0.20	<0.07	1.3	1.2	0.29	0.7	0.97	0.13	6.2
B- 9	0.10	<30	2.7	0.44	26	<0.13	<0.04	1.1	0.27	0.14	0.4	0.41	0.13	2.4
B-10	0.12	<34	1.8	0.74	26	<0.20	0.17	1.1	0.052	0.1	0.6	<0.015	0.86	2.8
B-11	0.10	108	6.4	<0.75	52	<0.26	0.38	1.9	0.11	0.19	13	0.076	0.71	11
B-12	0.12	<91	17	3.9	172	—	13	2.2	0.58	0.28	15	<0.033	0.99	11
B-13	0.11	<117	6.9	4.2	74	<0.26	0.79	1.4	0.17	0.20	14	<0.021	1.3	20
B-14	0.16	<120	12	4.2	76	<0.26	0.17	1.9	0.12	0.72	24	<0.017	1.2	9.6
B-15	0.15	<90	19	3.3	102	<0.28	0.17	1.1	0.14	0.62	26	<0.018	0.67	43
B-16	0.15	<78	24	4.2	102	<0.31	3.3	2.1	0.65	0.44	23	0.03	1.5	14
B-17	0.12	<102	16	2.6	82	<0.25	0.51	1.5	0.16	0.37	18	<0.020	1.3	8.9
B-18	0.13	<27	1.2	0.6	19	<0.19	0.44	0.4	0.083	0.40	0.2	<0.050	0.083	3.9
B-19	0.12	<19	1.1	0.6	18	<0.14	0.26	0.5	0.064	0.17	0.82	<0.015	0.035	3.8
B-20	0.11	<24	<0.82	0.5	18	<0.18		0.5	0.082	0.26	0.5	<0.018	0.092	6.9

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Table IX. (continued)

No.	Ba ppb→	Ce	Nd	Eu ($\times 10^{-3}$)	Gd	Yb ($\times 10^{-2}$)	Lu ($\times 10^{-3}$)	Hf ($\times 10^{-3}$)	Ta ($\times 10^{-3}$)	Hg	Th ($\times 10^{-3}$)	Sr ppm
B- 1	35	0.08	<0.30	4	<0.13	<4.3	18	<3.6	5.2	0.32	<5.5	0.27
B- 2	9.2	<0.041	<0.34	<1.4	0.20	<4.5	8.2	<4.1	<6.3	0.20	<6.6	0.14
B- 3	59	0.05	<0.29	1	<0.20	<2.4	2.5	<4.4	<5.7	0.3	<6.4	0.24
B- 4	31	<0.034	<0.11	1	<0.16	<4.0	2.7	<4.2	<7.6	0.15	<6.3	0.12
B- 5	11	0.1	<0.64	1	<0.17	—	27	<5.0	14	0.25	<8.4	0.20
B- 6	20	<0.030	<0.22	<0.86	<0.15	<1.8	3.7	<3.6	<6.1	0.43	<5.0	0.11
B- 7	17	<0.045	<0.19	<0.96	<0.12	<1.2	1.5	<3.3	<5.5	0.08	<4.3	0.049
B- 8	32	<0.039	<0.41	<1.2	<0.20	<1.9	<1.4	<5.6	18	0.2	<6.9	0.11
B- 9	18	<0.025	<0.18	<0.84	<0.13	<0.95	<0.81	<3.2	<5.8	0.08	<4.1	0.092
B-10	37	<0.037	<0.23	<1.4	<0.20	<1.3	<1.1	<4.5	<8.2	0.1	<6.1	0.096
B-11	5.7	<0.058	<0.57	<1.3	<0.26	—	14	<4.5	<9.0	0.2	<9.5	0.80
B-12	< 4.9	0.16	<0.78	<1.4	—	—	—	<7.6	11	1.1	<14	0.21
B-13	< 3.6	<0.054	<0.52	<1.3	<0.26	—	25	<5.8	<8.0	0.34	<9.1	0.14
B-14	12	0.07	<0.77	<1.3	<0.26	—	<8.1	19	<8.0	0.65	<11	0.17
B-15	7.6	0.2	<0.74	<1.1	<0.28	—	<10	<64	<7.4	0.60	<11	0.25
B-16	5.6	<0.070	<0.85	<1.5	<0.31	—	—	<7.6	<10	0.4	<14	0.20
B-17	< 9.6	0.1	<0.64	<1.5	<0.25	—	50	<6.2	<8.8	0.57	<10	0.12
B-18	14	<0.030	<0.21	1	<0.19	<0.71	<0.74	<4.1	595	0.060	<4.9	0.073
B-19	3.9	<0.025	<0.16	2	<0.14	<0.52	<0.46	<3.2	167	0.049	<3.9	0.035
B-20	28	—	<0.21	1	<0.18	<0.85	<0.83	<4.5	459	0.062	<5.1	0.11

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Table X. Arithmetic Mean Value and Standard Deviation of the Analysis (The values are given in ppb, except those expressed with ppm, and the standard deviation are in the parenthesis)

		Mikage	Uozaki	Nishinomiya	R. Sumiyoshi
pH		6.8 (0.3)	6.9 (0.1)	7.1 (0.2)	7.4 (0.04)
E. R.	ppm	281 (42)	158 (26)	307 (41)	88 (22)
Ca	"	42 (10)	29 (11)	51 (13)	18 (5)
Mg	"	5.7 (1.4)	3.5 (1.4)	7.3 (2.1)	1.6 (0.4)
Na	"	23 (6)	11 (3)	25 (6)	8.0 (0.7)
K	"	6.8 (2.8)	2.8 (1.1)	9.8 (1.8)	1.5 (0.5)
HCO ₃	"	96 (14)	64 (5)	109 (27)	49 (15)
Cl	"	28 (10)	10 (5)	35 (14)	5.4 (1.2)
SO ₄	"	40 (13)	17 (8)	39 (6)	9.1 (45)
SiO ₂	"	22 (5)	15 (2)	25 (5)	16 (3.3)
PO ₄	"	0.78 (0.73)	0.27 (0.46)	4.4 (1.9)	0.02
COD	ppm	0.54 (0.23)	0.22 (0.11)	1.4 (0.3)	0.53 (0.09)
BO ₃ -B		44 (11)	21 (3)	72 (24)	12 (6)
V		0.63 (0.29)	0.17 (0.06)	1.4 (0.3)	0.19 (0.06)
Fe		14.8 (3.7)	10.4 (3.6)	29.5 (27.2)	18.6 (13.1)
Fe*		3.1 (1.1)	1.9 (0.7)	6.2 (3.0)	6.0 (3.8)
Mn		3.2 (2.8)	1.2 (0.3)	2.4 (1.4)	3.2 (3.2)
Mn*		1.2 (0.6)	0.53 (0.15)	1.0 (0.5)	1.9 (1.6)
Cu		3.7 (1.3)	1.4 (1.1)	6.4 (5.1)	1.9 (1.0)
Cu*		2.3 (1.0)	0.84(0.65)	5.2 (4.6)	0.75 (0.20)
Zn		3.9 (3.0)	6.4 (2.8)	10.7 (3.7)	4.5 (1.6)
Zn*		5.9 (2.8)	4.2 (2.7)	8.0 (2.8)	2.5 (0.3)
Br		78 (27)	34 (15)	86 (38)	13 (6)
I		10 (7)	4.0 (2.5)	18 (8)	2.2 (1.5)
As		2.3 (1.5)	0.55 (0.13)	3.4 (1.0)	0.66(0.17)
Rb		3.6 (3.4)	0.60 (0.35)	17 (5)	0.73(0.51)
Cs	($\times 10^{-3}$)	5.8 (3.0)	3.2 (1.7)	17 (12)	4.9 (1.8)
Sr		194 (21)	91 (25)	270 (238)	73 (38)
Ba		41 (31)	27 (9)	15 (15)	22 (17)
Al		140 (35)	110 (19)	130 (21)	120 (18)
Sc	($\times 10^{-3}$)	8.7 (4.8)	2.2 (1.7)	19 (36)	20 (24)
Sb	($\times 10^{-2}$)	77 (63)	26 (23)	100 (39)	9.7 (9.3)
Cr		1.0 (0.7)	1.3 (1.2)	1.2 (0.8)	0.9 (1.4)
Se	($\times 10^{-2}$)	40 (32)	20 (10)	60 (33)	110 (160)
Co	($\times 10^{-2}$)	11 (6)	27 (37)	29 (30)	6.4 (1.5)

could be due to the similarity in the nature of the granite soils which cultivate the qualities of the underground water in the each district. Such similarity is very clearly expressed in a diagram, presented in Fig. 1, in which the milli-equivalent concentrations of the main components in the districts are plotted in radial.

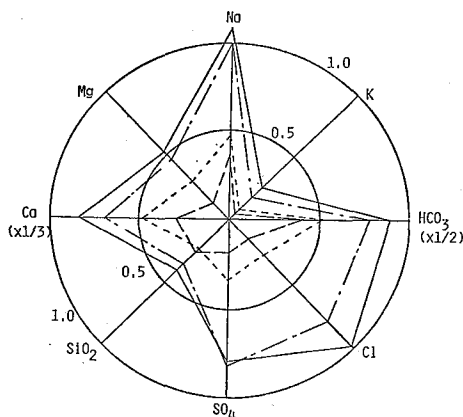


Fig. 1. Radial diagram of the concentration of major components (meq/l, except m mol/l of SiO_2)

-----; Mikage,; Uozaki,
 —————; Nishinomiya, ————; R. Sumiyoshi

3.2 Minor or trace components

Compared with the major components, the concentration variations of the minor or trace components between the well waters were large. In these components, it is possible to find out some character differences between the three districts, as follows.

(i) In PO_4 , BO_3 , V, I, As, Rb, Cs, Sc, and Se, there is an appreciably increasing tendency, that is Uozaki < Mikage < Nishinomiya.

(ii) Ba concentration is relatively high in Mikage.

(iii) In Br, Sr and Sb, Uozaki < Mikage = Nishinomiya.

In order to elucidate the dissolving processes or origins of the minor or trace components, it should be very important to compare their concentration ratios with the other environmental specimens. But, in present, it is regret that, in these components, enough informations are not available in various kinds of the specimens.

Concerning to the V/PO_4 ratio, Nishinomiya is $2\sim 3 \times 10^{-4}$. The values is comparable to 3.8×10^{-4} of the plankton (mainly, diatoms)¹¹⁾, 2.3×10^{-4} of Brown algae,¹¹⁾ 8×10^{-4} of Green algae¹²⁾ and so on.

The B/PO_4 ratio of Nishinomiya is approximately 1×10^{-2} . According to Bowen¹¹⁾, the values are 1.4×10^{-2} for Brown algae and 0.71×10^{-2} for Angiosperms. According to Yamamoto¹²⁾, the values are 2.0×10^{-2} for Green algae and 2.8×10^{-2} for Brown algae.

3.3 Concentration correlation

Using all the data presented in Tables VI~IX, the following correlation coefficients could be obtained; Na-Cl (0.95), BO_3 -Ca (0.94), V-Rb (0.93), V- PO_4 (0.92), Zn-Zn* (0.91), BO_3 - HCO_3 (0.90), HCO_3 -Ca (0.89), COD-Rb (0.87), Mn-Mn* (0.86), PO_4 -Rb (0.86), K-Rb (0.85), V-K (0.85), Cu-Cu* (0.85), V- SiO_2 (0.83), V-COD (0.83), Zn- BO_3 (0.83), Rb- BO_3 (0.82), I-COD (0.81), Fe*-COD (0.81), V-I (0.81), PO_4 -COD (0.80), HCO_3 -K (0.80), K-As (0.80), Mg-Ca (0.79), SO_4 -Mg (0.79), HCO_3 -Mg (0.79), BO_3 -K (0.79), K-Na (0.79), V-Cu* (0.79), HCO_3 -Br (0.79), BO_3 -Zn* (0.78), I-Rb

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(0.78), $\text{BO}_3\text{-SO}_4$ (0.77), $\text{SO}_4\text{-Ca}$ (0.77), K-Mg (0.77), K-Cl (0.77), Ca-As (0.76), $\text{Fe}^*\text{-Fe}$ (0.76), $\text{BO}_3\text{-PO}_4$ (0.75), $\text{BO}_3\text{-I}$ (0.75), $\text{PO}_4\text{-I}$ (0.75), I-As (0.75), V-Cs (0.74), K-COD (0.74), K- SiO_2 (0.74), $\text{PO}_4\text{-K}$ (0.74), K-Br (0.74), Ca-Br (0.74), V-Cl(0.73), Na-Mg (0.73), $\text{SiO}_2\text{-HCO}_3$ (0.73), K-I (0.73), $\text{PO}_4\text{-As}$ (0.73), $\text{SO}_4\text{-Na}$ (0.72), K-Ca (0.72), As- SiO_2 (0.72), Zn-I (0.72), COD- SiO_2 (0.72), $\text{SiO}_2\text{-Br}$ (0.72), $\text{SiO}_2\text{-Ca}$ (0.71), As-Rb (0.71), As- HCO_3 (0.71), Cl-Mg (0.71), $\text{BO}_3\text{-Na}$ (0.70), $\text{BO}_3\text{-SiO}_2$ (0.77), Cu-Ca (0.70).

Concerning to the PO_4 in Nishinomiya, which has been recognized as the most important minor components in the water for the *sake* brewing, a following correlation series was obtained; V (0.85), Al (0.76), Cs (0.65), I (0.59), As (0.52), SiO_2 (0.51), Sb (0.47), Rb (0.41), BO_3 (0.40), Fe (0.33), Se (0.30), SO_4 (0.28), Zn (0.28), K (0.26).

4. Origins of the components

By the multielement neutron activation analysis in co-operation with the chemical analysis, many informations, as mentioned above, on the chemical composition of the underground water samples have been obtained. But, in present, it is still difficult to conclude chemically the origin of the dissolved components, because of poor knowledge in the chemistry of the environmental soils which cultivate the water qualities.

But, based on a general principle that a pair of the components with a relatively high correlation coefficient has a similarity in their dissolving origins or processes, the following considerations on the origins have been made.

(i) In the dissolved components, three kinds of origin could be considered, that is from inorganic rocks and soils, and from biologically originated soils, and from sea water.

(ii) Ca, Mg, HCO_3 and SiO_2 should be dissolved from rocks and soils by the chemical action of CO_2 .

(iii) Na and Cl should be due to the permeation of sea water or the fallout.

(iv) PO_4 , V, I and As in *miyamizu* (Nishinomiya) should be the decomposition products of the ancient planktons or seaweeds flourished in an ancient gulf which is guessed to existed in the northern parts of the *miyamizu* district.

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REFERENCES

- (1) Y. Kusaka and T. Sagawa, *Memoirs of the Konan Univ., Science Series*, No. 16, Art. 87 (1973).
- (2) Y. Kusaka and T. Sagawa, *Nippon Kagaku Kaishi (J. Chem. Soc. Japan)*, No. 12, 2322 (1974).
- (3) Y. Kusaka, H. Tsuji, A. Morimoto, H. Ichiyama, S. Inukai, Y. Negoro, A. Takehara, and H. Tennojidani, *ibid.*, No. 10, 1363 (1978).

- (4) S. H. Harrison, P. D. LaFleur, and W. H. Zoller, *Anal. Chem.*, **47**, 1685 (1975).
- (5) T. Mamuro, Y. Matsuda, A. Mizohata, T. Takeuchi, and A. Fujita, *Ann. Repts. Radiation Center, Osaka Pref.*, **11**, 14 (1970); *Radioisotopes*, **20**, 111 (1971).
- (6) Y. Murata, S. Hirai, M. Okamoto, and H. Kakihana, *J. Radioanal. Chem.*, **36**, 525 (1977).
- (7) S. Susuki and S. Hirai, *Radioisotopes*, **26**, 799 (1977).
- (8) S. Hirai, *Bunseki*, No. 2, 83 (1979).
- (9) A. Mizohata and T. Mamuro, *Ann. Repts. Radiation Center, Osaka Pref.*, **17**, 16 (1976).
- (10) Y. Kusaka, H. Tsuji, Y. Tamari, T. Sagawa, S. Ohmori, S. Imai, and T. Ozaki, *J. Radioanal. Chem.*, **37**, 917 (1977).
- (11) H. J. W. Bowen, "*Trace Elements in Biochemistry*", Academic Press, New York, 1966, p. 68.
- (12) T. Yamamoto, *Kaiyo Kagaku (Marine Science)*, **1**, 226 (1969)