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Element profiles of onion producing districts in Japan, as determined using INAA and PGA

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We carried out instrumental neutron activation analysis (INAA) as well as k_0-based prompt gamma-ray analysis (k_0-PGA) to measure the amount of the elements in onions and studied whether the onions collected from different sites can be categorized based on the elemental concentration profile. Six elements (Na, Mg, Cl, K, Ca, Mn) and 3 elements (B, S, Cl) were measured by INAA and PGA in the onions grown in two districts, Hokkaido and Saga, in Japan, respectively. After principal component analysis, it was found that Cl was an important element to feature the producing districts of onions.

Introduction

Recently, consumer is paying high attention to the quality of agricultural crops, such as the production process or producing districts to verify the safety of the products. To know the producing district is one of the highest concerns to the consumers and is directly reflected to the market price. False labeling of the producing district is causing serious problems in agricultural products in Japan. Therefore, it is an urgent requirement to establish reliable scientific methods to analyze the producing district. In order to distinguish the districts, application of DNA marker, specific organic chemicals,[1,2] elemental concentration profile,[3,4] and stable isotopic ratios,[5] have been reported. When the cultivars are the same, there is no difference with DNA markers in plants even grown in different districts. Since plants growth is highly dependent on elemental concentrations in soil, elemental profile in a plant is expected to be correlated well with that of the soil. To determine elemental concentration in plants inductively coupled plasma-mass spectrometry (ICP-MS) is widely performed which requires acid digestion of the sample. However, some volatile elements such as I or Cl are lost during the sample preparation process.

To avoid the problem, it is preferable to apply a nondestructive analytical method that has no process of acid digestion. In this study, we performed INAA and PGA to determine the amount of elements, focusing on the elements that cannot be determined from acid digested sample. Then, we analyzed the producing district of the onions, grown in two major cultivating areas in Japan, Hokkaido and Saga, based on elemental concentration profile.

Experimental

Onion cultivars harvested from 14 and 20 points of Hokkaido and Saga, respectively, in 2003 were provided by Dr. ARIYAMA.[6] The domestic market share of the onions produced in Hokkaido and Saga were about 54% and 13%, respectively. Cultivars of onions and collected sites are shown in Fig. 1. The onions were prepared for activation analysis. After removing outer skins as well as bottom and upper parts, onions were washed well with pure water. Then, ten onions were homogenized and mixed well. It took one week to dry these samples at 60 °C.

Instrumental neutron activation analysis (INAA)

To perform INAA, 300–500 mg of the dried sample was doubly sealed in an ultra-pure polyethylene bag. Each bag with the sample was put in a polyethylene capsule (17 mm×31 mm) and was irradiated for 30 seconds by a research reactor, JRR-3, installed at the Japan Atomic Energy Agency (JAEA). The total thermal neutron dose was $5.7 \cdot 10^{14}$ n·cm^{-2}. Two minutes after irradiation, the gamma-rays emitted from the samples were measured for 180 seconds by a Ge counter (Canberra GX 1519). The gamma-ray energy used to determine ^{24}Na, ^{27}Mg, ^{38}Cl, ^{42}K, ^{49}Ca and ^{56}Mn were 1368, 1014, 1642, 1525, 3083 and 1811 keV, respectively.

Prompt gamma-ray analysis (k_0-PGA)

To perform k_0-PGA, about 500 mg of dried sample was doubly sealed in a FEP film bag and was suspended in the center of the PTFE frame by a PTFE wire. Then, the PTFE frame with the sample was set in a target box to which helium gas was introduced while irradiation.

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The PGA system was installed at the thermal neutron beam guide of the JRR-3. The emitted gamma-rays from the sample, during irradiation, were counted for 2,000 seconds by a Ge counter (Seiko EG&G). To calculate the elemental concentration, k_0-factors for B, K, Cl and S were applied.[7] Then the elemental concentration of B, Cl and S was calculated from the K concentration obtained by INAA.

Data analysis

Pirouette application software (ver. 3.11, Informetrix) was used for data analysis. The calculated data of elements was preprocessed by autoscale, that is, an average and variance were set as 0 and 1, respectively. Then, principal component analysis (PCA) was performed using the preprocessed data set, where the maximum factor was set as 3.

Results and discussion

In the case of INAA, 6 elements, Na, Mg, Cl, K, Ca and Mn were measured (Table 1). The amount of elements was shown as % or ppm (dry weight). By PGA, 6 elements, C, H, B, S, Cl and K were measured from 2,000 second counting. There was not any other gamma-ray detected from the other elements even the counting time was increased form 2,000 to 20,000 seconds. Four elements, B, S, Cl and K, were selected and the ratio of each elemental concentration to that of K, B/K, S/K and Cl/K, was calculated. Then, K concentration obtained by INAA was applied to calculate the concentration of B, S and Cl. Two elements, C and H were not used for the analysis because the amount of carbohydrates, consisted of C and H, was considered to be influenced by the way of growing rather than the soil type or the district.

Hokkaido		Saga	
No.	Cultivar	No.	Cultivar
H-1	A	S-1	C
H-2	A	S-2	C
H-3	A	S-3	C
H-4	A	S-4	C
H-5	A	S-5	C
H-6	A	S-6	D
H-7	A	S-7	D
H-8	B	S-8	E
H-9	A	S-9	E
H-10	A	S-10	F
H-11	A	S-11	G
H-12	B	S-12	H
H-13	B	S-13	I
H-14	A	S-14	D or G
		S-15	E
		S-16	E
		S-17	E
		S-18	E
		S-19	E
		S-20	E

Cultivar
A: KAIRYO-OKHOTSK No.1
B: SUPER KITAMOMIJI
C: SIPPO-WASE No.7
D: TAZAN
E: MOMIJI No.3
F: SIPPO-KAN70
G: SATSUKI
H: NEOEARTH
I: ANSWER

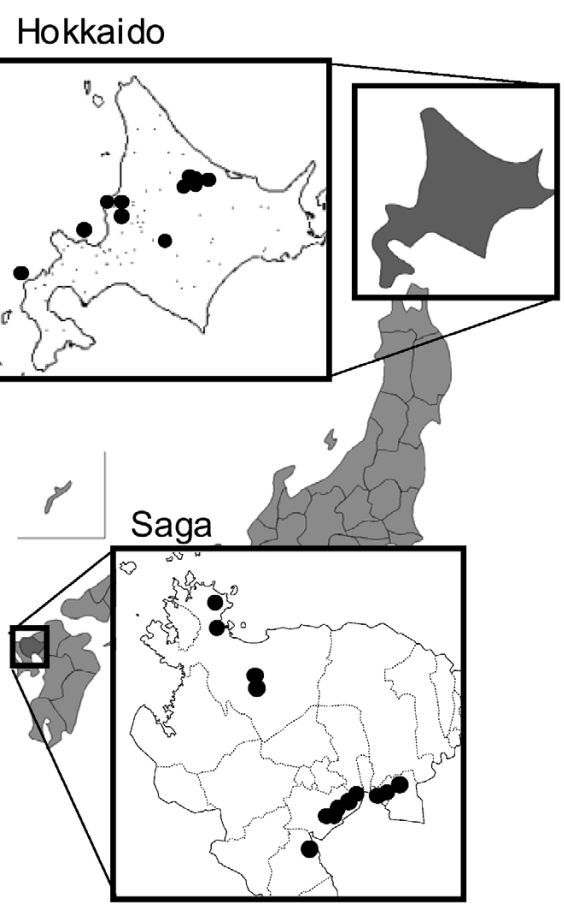

Fig. 1. Onion producing districts in Japan and onion cultivars. The onion sampling points are indicated. Two cultivars described as A and B were grown in Hokkaido, and 7 cultivars described as C, D, E, F, G, H and I were grown in Saga

Table 1. Elemental concentrations determined by INAA (a) and PGA (b)

(a)							(b)			
Sample No.	Na, %	Mg, %	Cl, %	K, %	Ca, %	Mn, ppm	Sample No.	B, ppm	S, %	Cl, %
H–1	0.011	0.096	0.138	1.41	0.165	10.1	H–1	10.1	0.471	0.132
H–2	0.012	0.125	0.127	1.69	0.160	11.2	H–2	16.9	0.441	0.131
H–3	0.007	0.117	0.122	1.49	0.173	10.9	H–3	10.5	0.574	0.124
H–4	0.006	0.142	0.045	1.45	0.138	11.1	H–4	11.1	0.463	0.043
H–5	0.009	0.103	0.119	1.48	0.119	10.5	H–5	10.4	0.407	0.117
H–6	0.011	0.110	0.177	1.52	0.195	10.2	H–6	13.3	0.466	0.170
H–7	0.011	0.130	0.143	1.82	0.138	10.7	H–7	13.3	0.564	0.146
H–8	0.010	0.123	0.145	1.52	0.205	8.6	H–8	10.2	0.489	0.133
H–9	0.011	0.103	0.114	1.59	0.155	8.2	H–9	14.9	0.374	0.109
H–10	0.024	0.111	0.108	1.25	0.140	8.9	H–10	11.7	0.315	0.076
H–11	0.008	0.138	0.041	1.37	0.149	16.4	H–11	9.9	0.338	0.029
H–12	0.014	0.117	0.088	1.45	0.172	12.5	H–12	6.0	0.451	0.067
H–13	0.008	0.101	0.119	1.68	0.212	7.3	H–13	12.1	0.477	0.119
H–114	0.009	0.109	0.098	1.45	0.145	8.2	H–14	12.3	0.325	0.100
S–1	0.012	0.081	0.151	1.11	0.141	6.8	S–1	5.9	0.338	0.137
S–2	0.010	0.078	0.105	1.31	0.047	21.6	S–2	6.9	0.302	0.093
S–3	0.009	0.106	0.128	1.43	0.111	8.5	S–3	7.3	0.255	0.117
S–4	0.016	0.070	0.199	1.22	0.158	9.0	S–4	4.9	0.270	0.175
S–5	0.008	0.088	0.165	1.30	0.133	11.6	S–5	8.3	0.320	0.150
S–6	0.007	0.086	0.127	0.99	0.147	10.8	S–6	7.5	0.367	0.121
S–7	0.007	0.088	0.150	1.20	0.167	13.7	S–7	7.0	0.405	0.146
S–8	0.011	0.094	0.142	1.09	0.137	8.2	S–8	10.3	0.334	0.134
S–9	0.008	0.083	0.146	1.21	0.081	8.1	S–9	3.7	0.296	0.135
S–10	0.005	0.094	0.109	1.29	0.128	11.5	S–10	7.8	0.425	0.107
S–11	0.008	0.079	0.125	0.94	0.161	9.2	S–11	5.2	0.283	0.107
S–12	0.008	0.080	0.104	1.07	0.176	8.4	S–12	7.9	0.188	0.100
S–13	0.007	0.073	0.115	0.96	0.146	16.0	S–13	3.6	0.365	0.103
S–14	0.008	0.078	0.154	1.27	0.207	23.6	S–14	5.8	0.467	0.148
S–15	0.012	0.092	0.143	1.10	0.226	16.5	S–15	10.2	0.457	0.136
S–16	0.016	0.111	0.214	1.24	0.245	9.7	S–16	7.7	0.414	0.211
S–17	0.016	0.106	0.173	1.26	0.190	12.6	S–17	15.9	0.495	0.175
S–18	0.022	0.125	0.192	1.34	0.124	11.8	S–18	13.0	0.352	0.195
S–19	0.023	0.123	0.223	1.30	0.135	11.0	S–19	12.3	0.432	0.227
S–20	0.012	0.108	0.171	1.39	0.109	10.8	S–20	10.0	0.550	0.170

The data set obtained by INAA and k_0-PGA was analyzed using PCA. The score plots of factor 1, 2 and 3 as well as factor 1 vs. factor 2 were shown in Figs 2 and 3, showing that the onion producing districts was almost totally separated between Hokkaido and Saga. When both data sets of INAA and k_0-PGA were applied for the analysis, the grouping of the onion producing districts was more clearly performed (Fig. 4). The modeling power, the power of variables for grouping the data, obtained from the data set of INAA as well as k_0-PGA is shown in Table 2. When the grouping is more effective, the modeling power is increased (the maximum value is 1). It was shown that the data of Cl was highly contributed for the modeling.

As is shown in Fig. 4, when INAA and k_0-PGA were performed, we could separate the onion production sites using 7 elements, B, S, Cl, Na, Mg, K and Ca. ARIYAMA et al.[6] reported the analysis of producing districts of onions collected from main production areas in Japan as well as those in abroad. Though the accuracy of grouping was close to 100%, they measured as many as 14 elements (Na, Mg, P, Mn, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Cs and Ba) by ICP-AES or ICP-MS.

Table 2. Modeling power of PCA modeling by data set of INAA and k_0-PGA in Fig. 4

Element – Method	Modeling power
B (ppm)–PGA	0.499
S (%)–PGA	0.537
Cl (%)–PGA	0.728
Na (%)–INAA	0.356
Mg (%)–INAA	0.545
Cl (%)–INAA	0.806
K (%)–INAA	0.467
Ca (%)–INAA	0.269
Mn (ppm)–INAA	0.207

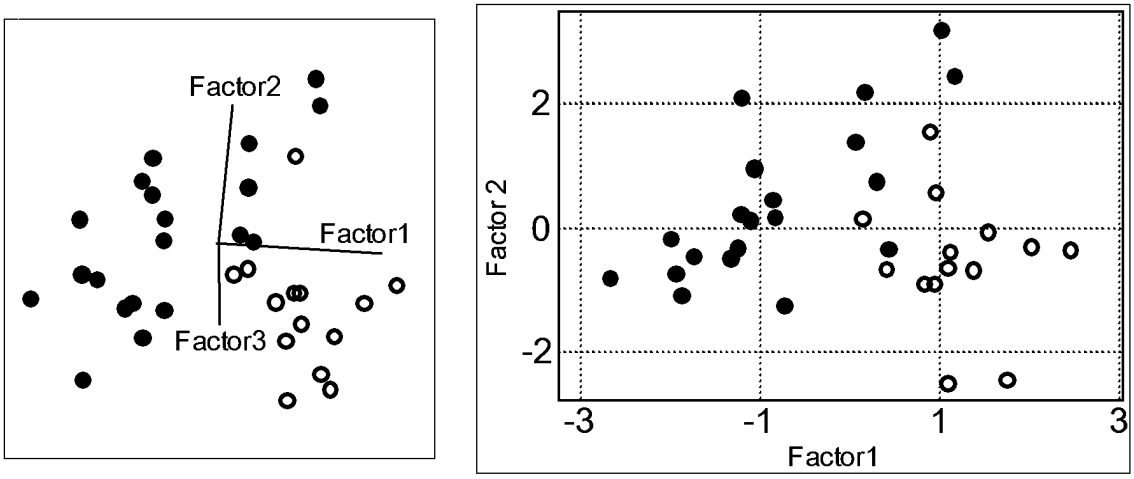

Fig. 2. Analysis by PCA with data set of INAA; ○ Hokkaido; ● Saga

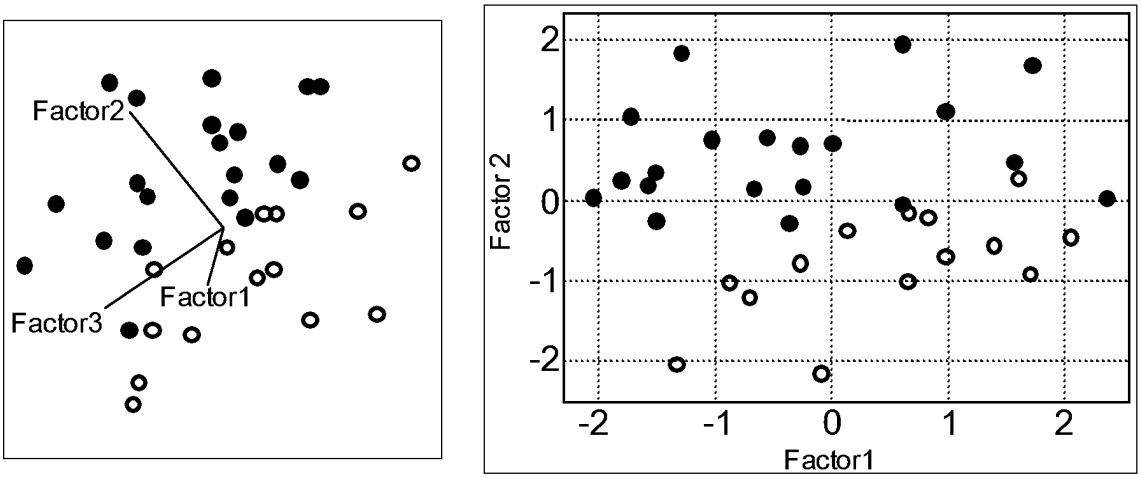

Fig. 3. Analysis by PCA with data set of k_0-PGA; ○ Hokkaido; ● Saga

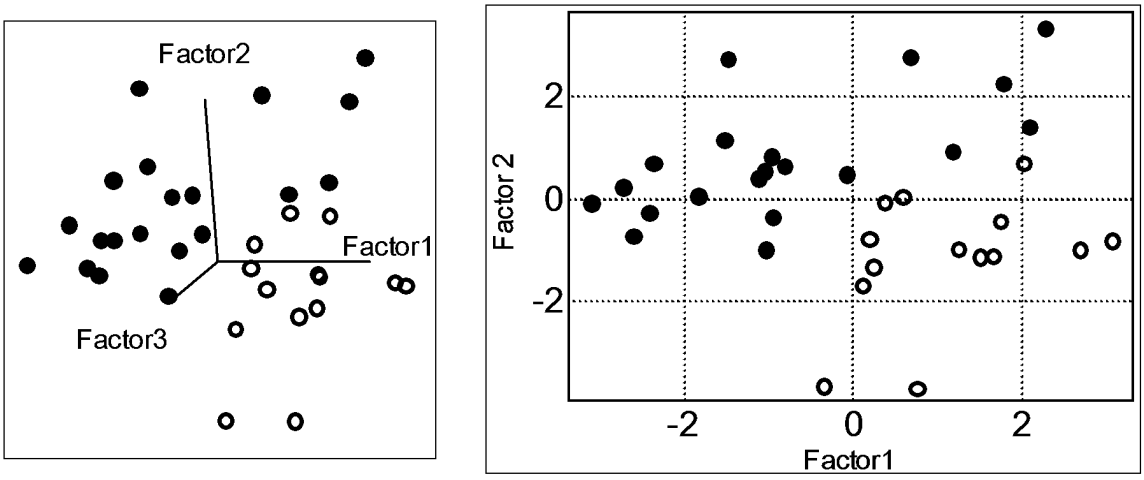

Fig. 4. Analysis by PCA with data set of INAA and k_0-PGA.;○ Hokkaido; ● Saga. The modeling power is shown in Table 2

Then, they concluded that the elemental analysis in onions can be used as a screening technique to estimate the producing district. However, the data of Cl amount whose modeling power was relatively high in our result was not available in their grouping process because it was necessary to digest samples with acids for the analysis. From our study, Cl concentration in onion was found to be an important factor to identify the producing district, which was able to measure because of using nondestructive methods, INAA and k_0-PGA.

The authors targeted the elements with relatively short half-lives in this study, since it takes relatively long time to measure the nuclides with longer half-lives, which was not practical for the survey work. Since INAA and k_0-PGA, which allow nondestructive analysis, can provide absolute amount of the elements, further application of these methods are expected to provide highly qualified information in determining the producing district.

Conclusions

This study is the first report to apply INAA and k_0-PGA to identify the producing district of agricultural crops from elemental concentration. The result showed that the producing district of onion was clearly separated by the data set of the elements determined by INAA and PGA. Among the elements measured, it was found that Cl, a difficult element to measure through digestion method, was a featuring element to identify producing district of onions.

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