

Neutron Activation Analysis of Korean Clays and Pottery

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Twenty trace elements were determined in 250 Korean potsherds and 5 clay samples by instrumental NAA. In the absence of identified samples of known origin, the potsherds were classified by a hierarchical centroid sorting method to construct a dendrogram. From this dendrogram 61 well-defined samples were selected to form 8 subclasses and five elements such as Cr, Cs, Sm, Sc and Th were supposed to be the main contributors for the classification. The 61 samples along with 5 clay samples were reclassified by means of minimal spanning tree as well as the hierarchical centroid sorting method by using 5 elements selected. As the results, the potsherds of certain classes defined in this work could be taken as a basis for latter identification and served as batches of identified species.

Introduction

Potsherds collected in Korea are supposed to be classified according to cultural bases into groups such as prehistoric, Kaya, Sinla, Baekje, Koryu and Rhee dynastic groups. It is of particular interest to take some conception about cultural exchange of early inhabitants through the study of potsherds. The characterization of ancient artefacts such as pottery has exclusively been left to some archaeological specialists. In this context, it is necessary to set up a scientific method to trace the geographical origin and classify according to function, use, the method of manufacture and the type of decoration.

For this purpose, physico-chemical method such as dilatometry, X-ray, etc. can be used.^{1,2} Through these methods, it has been found that the structure and texture depend on the nature of raw materials and techniques used for their fabrication. These methods are, however, limited because of small minerals formed during the cooking and bad crystallization.¹ It is supposed to be easier to characterize by using its trace element pattern, based on the assumption that it can be correlated with the clay from which it originated.^{1,3,4}

As the trace element contents have been used elsewhere to classify and identify archaeological specimens,^{5,6} it was considered possible that a similar study could establish the relationships between different clay source and pottery samples collected in Korea and could find out some pattern differences of trace elements to classify potsherds.

The neutron activation analysis was selected for the analysis of trace elements and was used as described previously.^{7,8} This method is known to be sufficiently sensitive for the determination of trace elements even below the parts per million levels and can be carried out non-destructively. Recent improvements in gamma-ray spectrometry made it possible to determine many elements simultaneously without loss of sensitivity.^{5,9}

Experimental

Apparatus. Gamma-ray spectrometry. Gamma-counting was done with a coaxial lithium-drifted germanium detector and a 4000-channel analyzer. System resolution was better than 2.0 KeV (FWHM at 1.33 MeV) with a peak-to-Compton ratio of 40:1. Punched paper tape output from the multichannel analyzer was fed to a CDC Cyber computer and computed for the decay-corrected peak areas as described previously.⁹

Sampling and pretreatments. As an essential preliminary, it is required to compile data on widely different potsherds and clay samples all over the country so as to extend the previous investigations^{7,8} and to enlarge the analytical data as wide a range of elements as possible.

About 250 samples of potsherds from different sites in Korea were collected through museums and five clay samples were collected directly. Potsherds were cleaned by washing with distilled water and dried at 110°C. An amount of 10–50 mg was tungsten-carbide-sawn from the body of each potsherd, *i.e.*, the surface and glaze material was eliminated. An accurate amount of each sample was weighed and sealed in a silica glass vial. Each clay sample was treated similarly after drying at 110°C.

Neutron activation analysis. Each silica glass vial was attached on its surface by a known amount of Au and Co as monostandards¹⁰. Use of two nuclides with different nuclear properties facilitates the evaluation of effective activation cross sections of all nuclides involved in activation for a given condition.^{12,13}

The vials were irradiated in the rotary specimen rack of TRIGA MARK III reactor for about 24 hrs. After irradiation the samples were allowed to cool for 1 day then the surface of each silica vial was cleaned with dilute nitric acid and the sealed vial was placed on a given geometry of the detector (the

background activity of the vial was negligible). The same vial was recounted at another given geometry for longer nuclides after 4 weeks' cooling.

Gamma-ray energy and peak areas were calculated by a Cyber computer as described above. Calculation of elemental contents was carried out as the procedure described in the previous papers^{10,11} by using flux index at the irradiation condition, nuclear data given in other papers^{12,13} and counting efficiency curves at given geometries.

Results and Discussion

Preliminary classification by single-linkage cluster analysis.

The No. of elements analyzed in this work was twenty elements, *i.e.*, Na, K, Sc, Cr, Fe, Co, Cu, Ga, Rb, Cs, Ba, La, Ce, Sm, Eu, Tb, Lu, Hf, Ta, Th (analyzed through ²³²Pa). Twenty elements in 250 potsherds result in 5,000 concentration values with an equal number of precision estimates.

The interpretation of this complex data usually requires samples of known origin and known to be similar to each other. From such a batch of identified specimens, one can define group limits for the concentration of trace elements and error associated with them. In the present work no such specimens exist. It was therefore necessary to perform a classification which involves the creation of classes among available samples before setting up criteria that would establish whether an individual sample belonged to the same or different class.

Many classification methods for a group of objects with limited number of common attributes (*e.g.*, elements) have been

suggested. A hierarchical centroid sorting method⁶ was chosen in this work.

One way of envisaging the procedure would be to consider trace-element concentrations of each sample as a point in a space of as many dimensions as trace elements determined. The various interpoint distances are used as a measure of dissimilarity. In this work, measures of dissimilarity were carried out by using following equation⁶:

$$D_{ij} = \frac{\sum_{n=1}^N |C_{i,n} - C_{j,n}|}{N}, \text{ where } N \text{ is the}$$

number of trace constituents; *i* and *j* the indices that identify a specific sample, and $C_{i,n}$ and $C_{j,n}$ the normalized concentration of element *n* in samples *i* and *j*. This normalization can avoid data with large numerical values from dominating the distance measure.

If *M* samples are considered, $M(M-1)/2$ different D_{ij} values can be calculated, the smallest of which corresponds to the most similar sample pair. The geometrical centroid of this pair was calculated and used for the pair such that only *M*-1 effective samples remain for which new D_{ij} values are calculated, among which the most similar pair is sought again. This process is repeated until all samples are incorporated into a single class. The resulting classification can be represented by a dendrogram. The computation was carried out by a Cyber computer. A dendrogram was thus constructed from about 250 potsherds as given in Figure 1. The length of vertical distance in the figure gives the degree of dissimilarity between individuals.

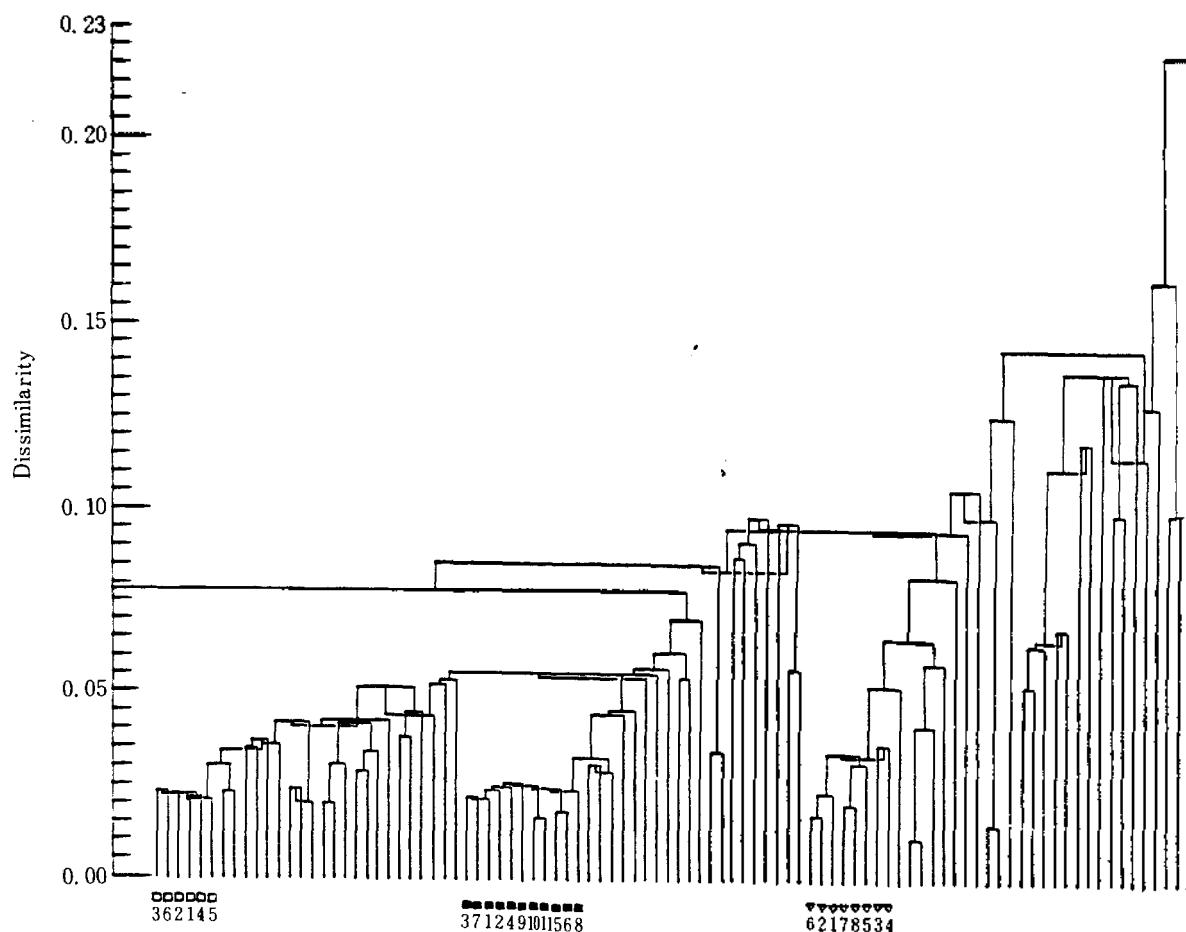


Figure 1. Dissimilarity dendrogram and the symbols are those defined in Table 1.

At the 16.4% dissimilarity level two subgroups were separated, the one consisted of a lone outlier and the other included a pair of samples. A subgroup consisting of 13 samples was further separated at 14.5% dissimilarity level. From the remaining suite of samples, three subgroups were separated, two are each consisted of a lone outlier and another included a pair of samples. At 9.6% dissimilarity level 15 samples were separated into a subgroup. Among those samples, some with smaller dissimilarity was selected to form a class and this is supposed to be used as a basis for latter identification. The reliability of the selection was improved with available informations such as excavation sites, color, decoration and *etc.* As shown in Figure 1 the formation of two distinct subgroups were found at 5.6% dissimilarity level. From the samples of each subgroup, a new selection of samples was done to form two classes for latter identification.

At the five lower dissimilarity levels, formation of five distinct subgroups was found from the remaining part of dendrogram which was not given in Figure 1 because of a limited space. Selection of samples was further carried out, forming 8 classes altogether.

Potsherds which forms each class in the dendrogram of Figure

1 have been found to be excavated from similar sites with some exception as shown in Table 1. In this table, the sites where the specimens of each class were found have been given together with the corresponding symbols used to the positions on the map shown in Figure 2 as well as the positions on the dendrogram in Figure 1.

Selection of Elements. Some important relative difference of trace element pattern was reported with the condition of the clay forming. Pre-processing of the clay consists in removal of the coarse material embedded in the clay and in addition of temper in order to prevent the clay from cracking when fired? The preprocessing and the variation in the manner of manufacturing will cause difficulties to find the object of the same population which is strictly identical. This points to limited significance of the similitudes and the differences in the observed element variations.

Distribution regularities and correlation patterns of some trace elements in clay were found to be transmitted and kept in pottery¹. A large variability and high degree of regularity in their distribution may be attributed to the structural characteristics of their ions and the influence of the crystal field¹.

For each class of samples which was set up by using Figure

TABLE 1: Archaeological Data of the Materials and Their Corresponding Symbols. The Sites for Clays are also Included

Symbol	Number of specimens	Sites		Item
▽	6	Kwangju	Kyonggi-do	White porcelain
	2	Yongin	Kyonggi-do	White porcelain
□	4	Yongi	Ch'ungch'ongnam-do	Punch'ong porcelain
	1	Kongju	Ch'ungch'ongnam-do	Punch'ong porcelain
	1	Kwangju	Chollanam-do	Punch'ong porcelain
△	4	Suwon	Kyonggi-do	Pottery
	3	Yoju	Kyonggi-do	Pottery
▲	7	Koryong	Kyongsangbuk-do	Pottery stand(3)
				Lid(2)
				Small pot(1)
				Flat-bottom pot(1)
▼	6	Koryong	Syongsangbuk-do	Small pot(3)
				Lid(2)
				Long-necked pottery(1)
X	5	Wando	Chollanam-do	Celadon bowl(2)
				Bowl(3)
○	5	Koryong	Kyongsangbuk-do	Small pot(3)
				Lid(1)
				Pottery stand(1)
	3	Suwon	Kyonggi-do	Pottery
	3	Ulchu	Kyongsangnam-do	Small pot
■	4	Kongju	Ch'ungch'ongnam-do	Punch'ong porcelain
	1	Yangju	Kyonggi-do	Celadon
	1	Kangjin	Chollanam-do	Celadon
	1	Taegu	Kyongsangbuk-do	Punch'ong porcelain
	1	Pusan	Kyongsangnam-do	Pottery
	1	Kyongju	Kyongsangbuk-do	Pottery
	1	Ongjin	Kyonggi-do	Pottery
	1	Yoju	Kyonggi-do	Pottery
①	1	Pusan	Chollabuk-do	Clay
②	1	Yoju	Kyonggi-do	Clay
③	1	Koryong	Kyongsangbuk-do	Clay
④	1	Haenam	Chollanam-do	Clay
⑤	1	Haenam	Chollanam-do	Clay

TABLE 2: Concentration of trace elements in Korea Potsherds (ppm). The symbols are defined in Table 1

Sample	Sm	Th	Cr	Cs	Sc	Sample	Sm	Th	Cr	Cs	Sc
V1	1.33	11.0	3.29	16.8	2.42	▼1	2.98	16.3	159	11.7	21.3
V2	1.72	10.2	2.46	13.9	2.53	▼2	3.85	15.9	109	8.95	15.1
V3	1.86	16.8	13.7	22.5	3.01	▼3	2.61	15.0	103	10.3	10.7
V4	2.03	14.7	8.00	14.1	3.18	▼4	2.45	16.3	115	11.5	15.5
V5	1.48	10.3	5.80	17.9	2.68	▼5	2.48	13.7	118	7.93	14.5
V6	1.33	11.2	9.45	11.6	2.11	▼6	3.18	16.0	157	9.22	17.3
V7	2.41	14.8	8.14	21.9	2.29	○1	2.17	16.3	99.8	4.04	11.5
V8	2.49	12.7	4.39	11.8	1.89	○2	2.74	15.7	91.0	8.03	13.2
□1	4.45	25.5	88.1	9.49	16.9	○3	2.52	15.4	107	5.57	15.3
□2	4.37	29.4	103	10.7	14.9	○4	1.89	12.8	102	4.92	9.63
□3	4.81	24.1	109	9.42	16.5	○5	2.09	13.4	107	5.46	11.9
□4	4.66	27.8	117	8.52	16.1	○6	2.04	10.9	81.6	3.04	8.74
□5	4.16	26.7	123	8.38	15.5	○7	2.76	13.1	110	6.08	13.2
□6	4.93	27.2	96.4	10.9	15.3	○8	2.62	13.9	114	6.77	13.9
△1	1.20	8.78	33.3	2.79	4.36	○9	2.31	18.4	96.6	6.19	14.8
△2	1.67	10.4	43.6	2.44	6.91	○10	2.08	14.7	86.7	6.16	13.6
△3	1.49	11.6	56.3	4.95	7.68	○11	2.47	18.5	89.9	7.67	15.2
△4	1.94	11.9	61.1	4.76	7.85	■1	3.70	21.8	100	7.27	11.9
△5	1.94	12.4	57.9	6.33	9.01	■2	3.67	22.3	81.7	9.09	12.0
△6	0.63	11.7	59.2	4.38	7.67	■3	3.78	19.8	97.1	8.74	14.3
△7	1.70	11.3	44.1	4.29	6.71	■4	3.60	22.5	94.3	9.26	13.6
▲1	2.83	12.0	80.6	7.25	10.3	■5	3.33	20.2	83.3	6.08	11.2
▲2	2.77	13.7	95.9	7.88	9.64	■6	2.56	21.7	80.3	5.89	11.1
▲3	2.71	14.3	87.3	7.87	10.6	■7	3.75	19.7	97.9	11.8	14.6
▲4	3.23	14.4	85.1	8.95	11.6	■8	2.11	20.9	76.3	4.94	13.4
▲5	3.08	13.9	78.8	7.89	11.7	■9	3.35	23.5	84.6	7.09	16.8
▲6	3.65	14.2	79.5	9.68	10.8	■10	3.37	20.7	81.9	2.56	13.6
▲7	2.43	12.9	85.0	7.94	9.94	■11	3.16	21.7	68.5	5.53	12.9
X1	6.55	37.2	218	13.7	34.9	①	5.47	33.1	156	11.5	26.2
X2	5.83	33.4	178	12.6	25.3	②	3.30	28.8	17.6	15.5	4.99
X3	6.10	38.7	213	12.9	30.5	③	6.01	32.6	166	10.9	26.7
X4	6.39	30.9	202	13.1	28.8	④	6.58	28.3	176	10.3	23.8
X5	6.04	29.2	185	10.7	27.9	⑤	4.39	25.9	103	17.4	19.6

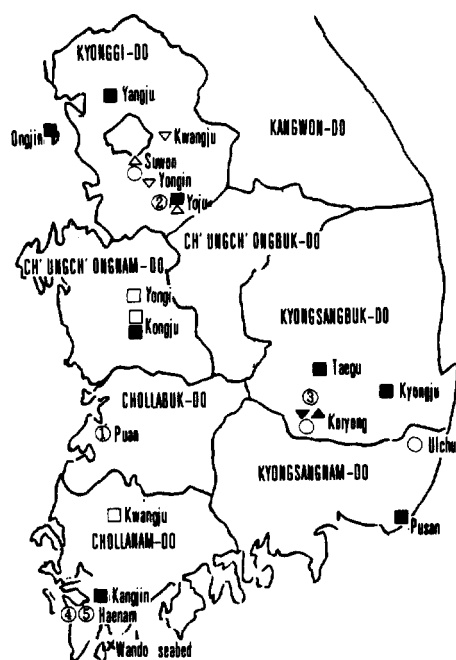


Figure 2. Map of Korea showing the sites at which samples were found. The sample symbols are defined in Table 1. Rings with numbers shows the sites at which clays were sampled.

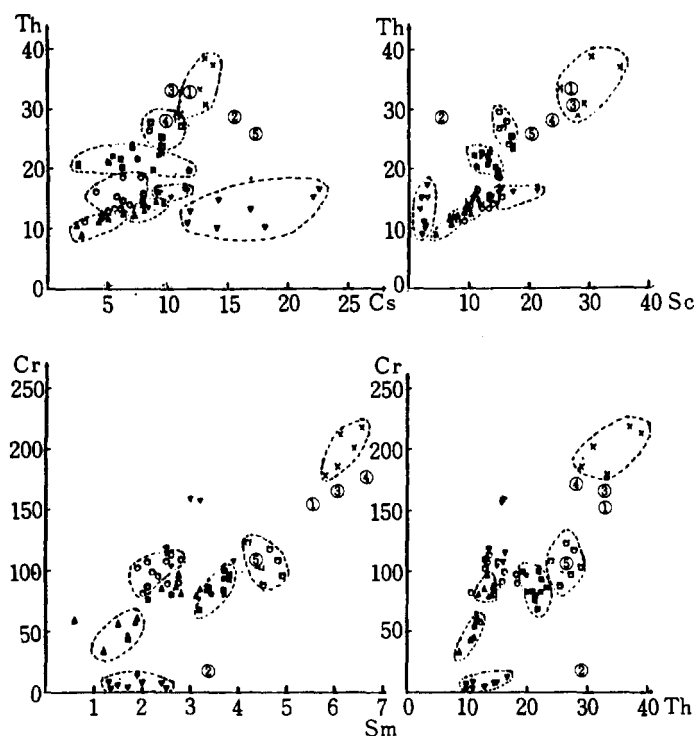


Figure 3. Examples of correlation. The symbols are defined in Table 1.

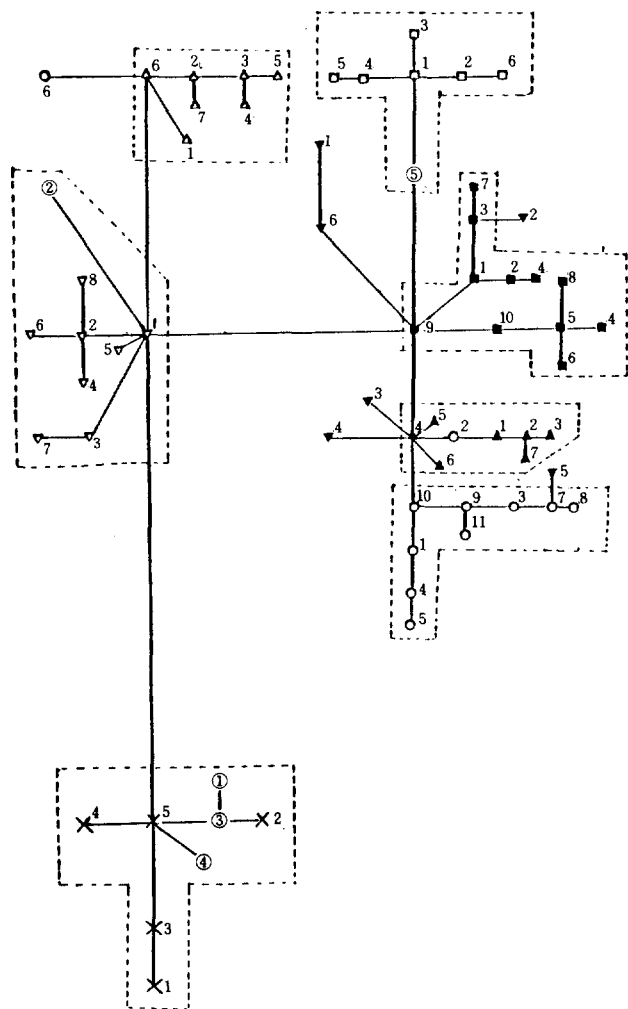


Figure 5. A diagram by means of MST by 61 potsherds and 5 clay samples. The symbols are defined in Table 1.

Clay 2 has been found to belong to the group symbolized ∇ as predicted above. Clay 5 belongs to the group symbolized \square , while clays 1, 3 and 4 belong together to the group symbolized \times . These results are on the contrary to the prediction by the geological nature as shown in Figure 2 and need further studies.

The same data are represented in 2 dimensions by means of a MST (Minimal Spanning Tree)^{14,15} which is shown in Figure 5. The interpoint distances concerned about MST are listed in Table 3.

The MST was constructed to establish a network of point-to-point links having the smallest possible total length. One of the points may be arbitrarily selected and connected to its nearest neighbour thereby creating an isolated fragment of the tree. This fragment is then connected to a nearest neighbour by the shortest available link and the process is continued until all points have been similarly linked. It should be stressed that Figure 5 which

is drawn to scale the nearest neighbour distances can not be used to measure other interpoint distances.

In the diagram in Figure 5 the group symbolized ∇ is destroyed as in Figure 4 and two samples of the class symbolized \circ change the positions, while other samples remain in their original groups. Clay samples remain in the same way as in Figure 4. The dendrogram in Figure 4 and the diagram in Figure 5 show the presence of some well-defined groups of samples. e.g., two groups symbolized ∇ and \triangle in Kyonggi-do, the group symbolized \square in Chungchongnam-do, the group symbolized \times in Chollanam-do and the group symbolized \blacktriangle in Kyongsangbuk-do. The figures also show that other two groups are in relatively well-defined groups which, nevertheless, exhibit within-group variation, e.g., the groups symbolized \blacksquare and \circ . This indicates the existence of early inhabitants in the excavated areas who tended to move around large areas.

In conclusion, the potsherds of certain classes defined in this work could be taken as a basis for latter identification and served as batches of identified species.

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