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Characterization of Korean Clays and Pottery by Neutron Activation Analysis (III). A Classification Rule for Unknown Korean Ancient Potsherds

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A number of Korean potsherd samples has been classified by Fisher's discriminant method for the training set of Kyungki, Koryung and Kyungnam groups. The Koryung samples have been further classified for the training set of Koryung A, B and C subgroups. The training sets have been used to define classification of unknown samples and clay samples so as to find out some similarity between clay samples and certain potsherd groups.

Introduction

The pattern recognition (PR) approach can be stated as follow,[1-3] "Given a set of objects and a list of measurements made on them, it is possible to find or predict a property of the objects, that is not directly measurable but is known to be related to the measurements via some unknown relationship." Archaeology is one of the major beneficiaries of such a PR approach,[4,5] the other notable area of application being environmental science,[6] forensic science[7] and diagnostic classification.[8]

In pattern recognition, two different situations can be considerecd according to whether the calsses into which individual samples must be classified are known or not. In the first instance, one speaks of supervised learning and in the second of unsupervised learning. Only supervised learning is of interest here. Supervised learning means that a learning or training set, *i.e.*, a number of classified individuals or samples, is developed, and this is used to define a classification rule which is subsequently applied to the classification of unknown samples.[8]

In the previous work, some classification had been tried

Table 1. Samping Sites and Their Corresponding Symbols for Potsherd and Clay Samples

Symbols	Number of samples	Sites		Items
△	4	Kwangju	Kyungki-do	pottery
△	17	Suwon	Kyungki-do	pottery
△	8	Yoju	Kyungki-do	pottery
△	2	Amsa-dong	Seoul	pottery
△	3	Yoksam-dong	Seoul	pottery
▲ (▽)	19	Koryung A	Kyungsangbuk-do	pottery
▲ (▼)	15	Koryung B	Kyungsangbuk-do	pottery
▲ (×)	4	Koryung C	Kyungsangbuk-do	pottery
○	9	Kimhae	Kyungsangnam-do	pottery
○	7		Pusan	pottery
①	1	Yoju	Kyungki-do	clay
②	1	Koryung C	Kyungsangbuk-do	clay
③	1	Wolsung	Kyungsangbuk-do	clay
④	1	Wolsung	Kyungsangbuk-do	clay
⑤	1	Wolsung	Kyungsangbuk-do	clay
⑥	1	Wolsung	Kyungsangbuk-do	clay
⑦	1	Kwangju	Kyungki-do	clay

to create some training set of potsherds by means of a hierarchical centroid sorting,[4] a minimal spanning tree,[4] principal component analysis[5] and Fisher's discriminant analysis.[9]

This paper reports on the work done in the development of classification rules for the unknown Korean ancient potsherds. It is an extension of the Fisher's discriminant analysis which had been carried out previously.[9] The relationships between clay sources and potsherds collected from various sites in Korea have been studied here on the basis of elemental abundances obtained by neutron activation analysis.

Description and Analysis of Samples

Samples of potsherds from different sites in Korea were collected through museum and clay samples were collected directly. In Table 1, the sites where the samples were found, are given together with the corresponding symbols. The whole samples were grouped into three classes according to geographical similarity as shown in Table 1. The samples found in Koryung were further grouped into three subclasses according to sites, using the symbols in parenthesis as shown in Table 1.

The elemental analysis of potsherds was carried out by thermal neutron activation analysis. The detailed analytical procedures had been described elsewhere.[4]

Results and Discussion

Twenty elements, *i.e.*, Na, K. Sc, Cr, Fe, Co, Cu, Ga, Rb, Cs, Ba, La, Ce, Sm, Eu, Tb, Lu, Hf, Ta, and Th utilising neutron activation technique, have been used in the present PR study for the classification of potsherds collected from various sites as shown in Table 1.

The classification into groups using different symbols as shown in Table 1 has been found to be mainly attributed to 11 elements[9] such as Cu, K, La, Na, Ce, Th, Cr, Cs, Sc, Rb and Co.

Using the data set of the selected elements, $W^{-1}B$ matrix has been generated,[9] where W and B are the total within-group sum of squares and cross products (SSCP) and the pooled between-group SSCP matrix, respectively.[9] Since a three-fold classification problem is involved in this case, two discriminant functions have been computed. The discriminant scores for individual i along the optimal discriminant function axes f_1 and f_2 have been generated as described previously.[9]

A map has been drawn for the individuals of the three groups and for the corresponding group centroids in a 2-dimensional discriminant space together with a territorial diagram of each group. The overlap between groups in the diagram could be attributed to the location of some samples in contrast to the geographical prediction based on excavated sites. Refined training set of each group has been formed by eliminating such samples so as to perform more efficient classification. The discriminant scores for individual *i* which correspond to eigen values L_1 and L_2 have been generated for the Kyungki, Koryung, and Kyungnam potsherds[8,9] as follows:

$$\begin{aligned} &L_1 = 5.036 \\ &DS_{1,i} = 0.335z_{Cu,i} - 0.143z_{K,i} - 0.258z_{La,i} + 0.213z_{Na,i} \\ &\quad - 0.266z_{Ce,i} + 0.074z_{Th,i} - 0.706z_{Cr,i} - 0.191z_{Cs,i} \\ &\quad + 0.341z_{Sc,i} - 0.021z_{Rb,i} - 0.167z_{Co,i} \end{aligned}$$

$$\begin{aligned} &L_2 = 1.468 \\ &DS_{2,i} = 0.732z_{Cu,i} + 0.011z_{K,i} + 0.073z_{La,i} - 0.249z_{Na,i} \\ &\quad + 0.244z_{Ce,i} - 0.170z_{Th,i} - 0.058z_{Cr,i} + 0.504z_{Cs,i} \\ &\quad - 0.115z_{Sc,i} - 0.195z_{Rb,i} + 0.020z_{Co,i} \end{aligned}$$

Instead of the standardized Z values, the raw data can be used. For this purpose, the weight coefficients have been converted in such a way that the final discriminant scores remain unchanged.[8] Discriminant scores for individual *i* thus obtained are given as follows:

$$\begin{aligned} DS_{1,i} = {} & 9.68\times10^{-3}x_{Cu,i} - 5.22\times10^{-5}x_{K,i} - 2.15\times10^{-2}x_{La,i} \\ & + 9.47\times10^{-5}x_{Na,i} - 7.85\times10^{-3}x_{Ce,i} + 2.03\times10^{-2}x_{Th,i} \\ & - 1.83\times10^{-2}x_{Cr,i} - 7.64\times10^{-2}x_{Cs,i} + 8.14\times10^{-2}x_{Sc,i} \\ & - 5.63\times10^{-4}x_{Rb,i} - 1.36\times10^{-2}x_{Co,i} + 1.48 \end{aligned}$$

$$\begin{aligned} Ds_{2,i} = {} & 2.12\times10^{-2}x_{Cu,i} + 4.02\times10^{-6}x_{K,i} + 6.08\times10^{-3}x_{La,i} \\ & - 1.11\times10^{-4}x_{Na,i} + 7.02\times10^{-3}x_{Ce,i} - 4.67\times10^{-2}x_{Th,i} \\ & - 1.51\times10^{-3}x_{Cr,i} + 2.02\times10^{-1}x_{Cs,i} - 2.74\times10^{-2}x_{Sc,i} \\ & - 5.24\times10^{-3}x_{Rb,i} + 1.63\times10^{-3}x_{Co,i} - 2.64 \end{aligned}$$

Moreover, it is necessary to know whether only one or both of discriminat functions are statistically significant. As a first approximation, the χ^2-statistics (Barlett's V) is computed by taking into account both discriminant functions:[8]

$$V = [N - 1 - (R + K)/2]\ \ln(1 + L_1)\ (1 + L_2),$$

where N, R and K are numbers of whole individuals, selected elements and groups, respectively. Substituting each number, the V value is obtained

$$V = [87 - 1 - (11 + 3)/2]\ \ln(1 + 5.04)\ (1 + 1.47) = 213.5$$

$$d.f. = R(K - 1) = 11 \times (3 - 1) = 22$$

For significance level $\alpha = 0.001$, χ^2 equals 48.27. Thus, it is found that the V value exceeds the significance level 0.001 of the χ^2 distribution with 22 degrees of freedom which is

Table 2. Allocation of a Clay sample by the Mahalonobis Distance Classifier

	DS_1	DS_2	
Centroid of	0.602	−0.353	$A_c = [(-0.584-0.602)^2+(-1.41+0.353)^2]^{1/2} = 1.59$
kyunki	−1.06	0.202	$B_c = [(-0.584+1.06)^2+(-1.41-0.202)^2]^{1/2} = 1.68$
koryung	1.17	0.284	$C_c = [(-0.584-1.17)^2+(-1.41-0.284)^2]^{1/2} = 2.44$
kyungnam	−0.584	−1.41	
Clay sample	(a priori known to be Kyungki)		
Classification; Clay sample is assigned to the region of Kyungki; $A_c<B_c$ and $A_c<C_c$.			

Table 3. Prediction Results for the Kyungki, Koryung, and Kyungnam Potsherds

A priori group membership	Number of samples	A posteriori (predicted) group membership		
		Kyungki	Koryung	Kyungnam
Kyungki	34	27(31%)	5(5.7%)	4(4.6%)
Koryung	37	1(1.1%)	32(37%)	2(2.3%)
Kyungnam	16	6(6.9%)	0(0.0%)	10(11%)

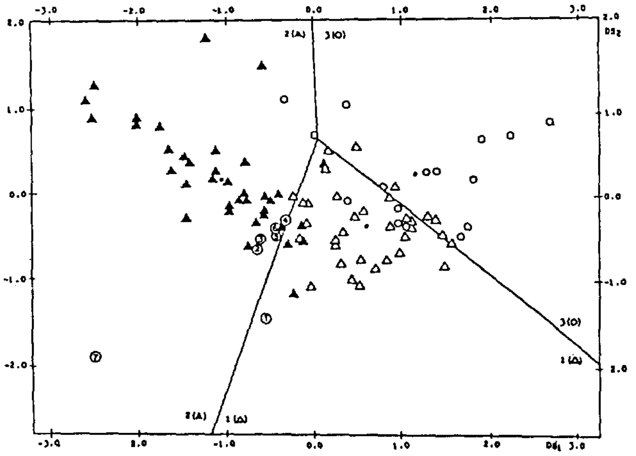

Figure 1. Plot and terriotrial map of discriminant score 1 versus discriminant score 2 for the Kyungki, Koryung, and Kyungnam potsherds and clay samples. (•) Group centroid; 1 (Δ) Kyungki; 2 (▲) Koryung; 3 (O) Kyungnam.

48.27. Therefore, the hypothesis is accepted that the differentiation among the groups (Kyungki, Koryung, and Kyungnam) on the basis of both discriminant functions is significant and not due to chance or sampling errors.

The next step is to identify whether the differentiation among the groups is due to one or both discriminant functions. For this, Barlett's V is computed and tested after removal of function f_1. The approximate χ^2-statistics which takes into account the second discriminant function f_2 is computed as follows:

$$\begin{aligned}V - V_1 &= 213.5 - [N - 1 - (R+K)/2]\ \ln(1+L_1)\\ &= 213.5 - (86-7)\ \ln(1+5.04)\\ &= 71.44\\ \text{d.f.} &= R(K-1) - (R+K+2S) = 11(3-1) - (11+3-2) = 10,\end{aligned}$$

where S defines the number of nonzero eigenvalues which is 1 in this case. For significance level 0.001, χ^2 equals 29.59. Since $V - V_1$ exceeds the significance level 0.001 of χ^2 distribution with 10 degrees of freedom which is 29.59, the hypothesis is accepted that both discriminant fanctions contribute significantly to the differentiation among 3 groups of potsherds. Consequently both functions are retained for further analysis.

Figure 1 shows a map of the individuals of the three groups and the corresponding group centroids in the 2-dimensional discriminant space with a territorial diagram of each group. The territorial diagram contains linear boundaries drawn orthogonally at half the distance between each pair of group centroids. Graphically, the classification rule can be formulated as follows: assign sample i to Kyungki group if it falls into region 1 or on the boundary 1/3; or to Koryung group if it falls into region 2 or on the boundary 1/2; or to Kyungnam group if it falls into 3 or on the boundary 2/3.

Practically, a classification rule may be used as follows: assign sample i to the group whose centroid is nearest to that individual. On the other hand, sample i can be classified according to its position DS_i on the discriminant axis as compared to the position of centroids $\overline{DS}_p$ and $\overline{DS}_q$ of group p and q, respectively. In the present work, this classification rule can be described as follows: assign sample i to Kyungki group if $A_C \leqslant B_C$ and $A_C < C_C$; Koryung group if $B_C \leqslant C_C$; and $Bc < Ac$; Kyungnam group if $C_C \leqslant A_C$ and $C_c < B_c$, when

$$\begin{aligned}A_C &= [(DS_{1,c} - \overline{DS}_{1,Kyungki})^2 + (DS_{2,c} - \overline{DS}_{2,Kyungki})^2]^{1/2}\\ B_C &= [DS_{1,c} - \overline{DS}_{1,Koryung})^2 + (DS_{2,c} - \overline{DS}_{2,Koryung})^2]^{1/2}\\ C_C &= [(DS_{1,c} - \overline{DS}_{1,Kyungnam})^2 + (DS_{2,c} - \overline{DS}_{2,Kyungnam})^2]^{1/2}\end{aligned}$$

This classification corresponds to Mahalonobis distance classifier discussed by Coomans and Massart[8]. Table 2 gives an example for the clay sample ①.

The above classification procedure has been applied to all postsherd samples which had been used for the training sets and the number of correctly classified individuals has been determined. Written as a percentage, this expresses the efficiency of the classification procedure. The classification results are shown in Table 3. It should be noted that when this method is used, 79% of 87 potsherd samples has been correctly classified.

The above classification procedure has been applied to classify Koryung samples into three subgroups as shown in Table 1, *i.e.*, Koryung A, B and C, which are based on geographical difference. For this purpose, elements have been selected as described above. The results showed that differentiation between subgroups was attributed mainly to 8 elements, namely, Sm, Ga, La, Cs, Tb, Sc, Rb and Fe. The discriminant scores for individual i which correspond to eigen values L_1 and L_2 have been generated after refining the train-

Table 4. Allocation of a Clay sample by the Mahalonobis Distance Classifier

	DS_1	DS_2	
Centroid of			
Koryung A	1.57	-0.0642	$A_C=[(-3.51-1.57)^2+(-0.932+0.0642)^2]^{1/2}=5.15$
Koryung B	-1.20	0.552	$B_C=[(-3.51+1.20)^2+(-0.932-0.552)^2]^{1/2}=2.75$
Koryung C	-2.95	-1.76	$C_C=[(-3.51+2.95)^2+(-0.932+1.76)^2]^{1/2}=1.00$
Clay sample	-3.51	-0.932	
		(a priori known to be Koryung C)	
Classification; Clay sample is assigned to the region of Koryung C; $C_c<A_c$ and $C_c<B_c$.			

Table 5. Prediction Results for the Subgrouping of Koryung Potsherds

A priori group Membership	Number of samples	A posteriori (predicted) group membership Koryung A	Koryung B	Koryung C
Koryung A	19	18(47%)	3(7.9%)	0(0.0%)
Koryung B	15	1(2.6%)	12(32%)	1(2.6%)
Koryung C	4	0(0.0%)	0(0.0%)	2(7.9%)

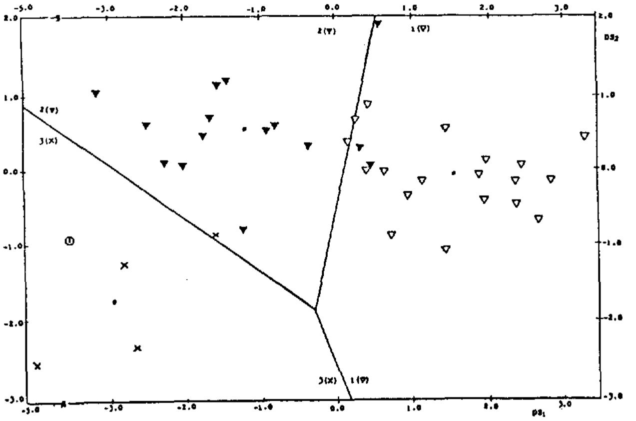

Figure 2. Plot and territorial map of discriminant score 1 versus discriminant score 2 for the subgrouping of Koryung potsherds and clay sample. (•) Group centroid; 1 (∇) Koryung A; 2 (▼) Koryung B; 3 (×) Koryung C.

ing set of each subgroup as described above. The final results are as follows:

$$L_1=5.457$$

$$\begin{aligned}DS_{1,i}= & -3.61\times10^{-1}x_{Sm,i}-6.28\times10^{-2}x_{Ga,i}-3.54\times10^{-3}x_{La,i}\\ & -1.22\times10^{-1}x_{Cs,i}-5.35\times10^{-1}x_{Tb,i}-6.28\times10^{-2}x_{Sc,i}\\ & -1.52\times10^{-2}x_{Rb,i}-7.18\times10^{-5}x_{Fe,i}+6.93\end{aligned}$$

$$L_2=2.176$$

$$\begin{aligned}DS_{2,i}= & 5.82\times10^{-2}x_{Sm,i}+4.76\times10^{-2}x_{Ga,i}-4.82\times10^{-2}x_{La,i}\\ & +1.74\times10^{-1}x_{Sc,i}+7.69\times10^{-1}x_{Tb,i}-1.29\times10^{-1}x_{Sc,i}\\ & -6.93\times10^{-3}x_{Rb,i}-1.26\times10^{-6}x_{Fe,i}+1.18\end{aligned}$$

It was confirmed by the procedure described above that the hypothesis is accepted that both discriminant functions contribute significantly to the differentiation among subgroups.

Figure 2 shows a map of the individuals of the three subgroups and the corresponding group centroids in the 2-dimensional discriminant space with a territorial diagram of each group. In this case, the classification rule can be described as follows: assign sample *i* to Koryung A if $A_C \leqslant B_C$ and $A_C<C_C$; Koryung B if $B_C \leqslant C_C$ and $B_C<A_C$; Koryung C if $C_C \leqslant A_C$ and $C_C<B_C$,

when

$$\begin{aligned}A_c&=[DS_{1,c}-\overline{DS}_{1,Koryung\ A})^2+(DS_{2,c}-\overline{DS}_{2,Koryung\ A})^2]^{1/2}\\ B_C&=[(DS_{1,c}-\overline{DS}_{1,Koryung\ B})^2+(DS_{2,c}-\overline{DS}_{2,Kolryung\ B})^2]^{1/2}\\ C_C&=[(DS_{1,c}-\overline{DS}_{1,Koryang\ C})^2+(DS_{2,c}-\overline{DS}_{2,Koryung\ C})^2]^{1/2}\end{aligned}$$

The above classification rule which corresponds to Mahalonobis distance classifier has been applied to a clay sample ② and the results are shown in Table 4. The classification procedure has been applied to all Koryung samples in Table 1 which had been used for the training set and the number of correctly classified individual has been determined. The classification results are shown in Table 5, which shows that 87% of 38 potsherds is correctly classified.

Six clay samples, which are supposed to have served as source material of pottery were included in Figure 1 to differentiate them among groups. One clay sample was included in Figure 2 for the same purpose. Figure 1 shows that clay ① is allocated to Kyungki group, whereas clay ②-⑥, which were sampled from Koryung and Wolsung are allocated to Koryung group. Figure 2 shows that clay ② is allocated to Koryung C subgroup. All these results are in accord with the geographical prediction based on excavated sites of potsherds and sampling sites of clay. The results suggest that the clay samples served as source material for potteries excavated in vicinity sites. The clay ⑦ taken from Kyungki which is supposed to have served as source material of porcelain shards was, however, allocated in contrast to the geographical prediction as shown in Figure 1. This shows that the classification procedure developed here for potsherds could not be used for the classification of porcelain shards.

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The Synthesis of *p*-acetylcalix[4]arene via Fries Rearrangement Route

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Starting with the readily available *p-tert*-butyl-calix[4]arene 2, *tert*-butyl groups are removed by $AlCl_3$-catalyzed de-alkylation reaction, and the calix[4]arene 3 formed is converted to the tetraacetate 4. This compound undergoes Fries rearrangement to yield *p*-acetylcalix[4]arene 6, which seems to be an attractive starting material for the introduction of functional groups. As a preliminary experiment *p*-(1-hydroxyethyl)calix[4]arene 7 is prepared by $LiAlH_4$ reduction of 6.

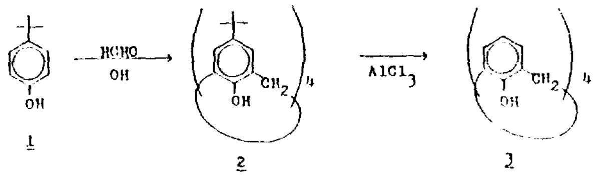
Introduction

Calixarenes which have various functional groups are attractive with respect to the long term goal of calixarene research, *viz.* the construction of enzyme models. *p-tert*-Butylcalix[4]arene 2 has become one of the most accessible of all the known macrocyclic cavity-containing compounds, obtainable in the yield[1,2] greater than 50% from the base induced condensation of *p*-butylphenol and formaldehyde. $AlCl_3$-catalyzed de-*tert*-butylation has been shown to proceed in excellent yield,[3] making calixarene 3 an extremely attractive starting material for the preparation of various para-functionalized calix[4]arenes.

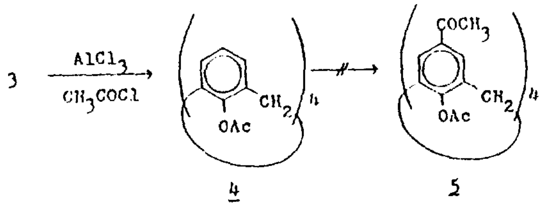
Direct introduction of functional groups into the calixarene via electrophilic substitution has been attempted in several laboratories, however, failed in most cases. The limited successes that have been published are the sulfonation of calix[6]arene by Shinkai and coworkers,[4] the bromination of calix[4]arene by Gutsche and coworkers,[5] and the nitration of calix[4]arene in our laboratories.[2]

Due to the carbonyl group can be converted to various functional groups by several ways such as oxidation, reduction, Grignard reaction and Wittig reaction, we repetitiously attempted to introduce carbonyl function into the para positions of calix[4]arene 3 *via* Friedel-Crafts acylation reaction and Reimer-Tieman reaction. To our disappointment, however, all the attempts failed. Friedel-Crafts conditions resulted in O-acylation rather than *para*-acylation, and the resulting esters failed to undergo further reaction at the para positions. Gutsche and coworkers also reported the same results.[6]

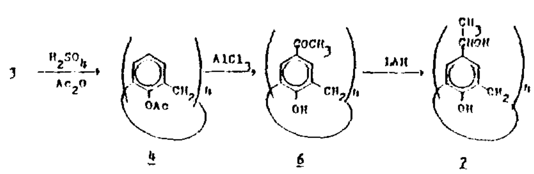
When calix[4]arene 3 was treated with Reimer-Tieman condition, only unidentified products were resulted without any indication of introduction of aldehyde groups into the para positions of calix[4]arene. Recently Gutsche and coworker[6] reported the preparation ot the methyl ether of *p*-carboxycalix[4]arene starting from *p*-bromocalix[4]arene obtained by bromination of the calix[4]arene followed by lithiation and carbonation. In the similar fashion, they prepared the methyl ether of *p*-acetylcalix[4]arene by Friedel-Craft acylation of the methyl ether of calix[4]arene.



Scheme 1



Scheme 2



Scheme 3

As an alternate route for the introduction of carbonyl functions into the para positions we explored the Fries rearrangement route. In Fries rearrangement,[7] phenol esters rearrange in the presence of metal halide catalysts to form *ortho*- or *para*-hydroxy ketons depending upon steric and temperature factors. Since all the ortho positions in calix[4]arene are oc-