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Characterization of Korean Porcelainsherds by Neutron Activation Analysis

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Some pattern recognition methods have been used to characterize Korean ancient porcelainsherds using their elemental composition as analyzed by instrumental neutron activation analysis. A combination of analytical data by means of statistical linear discriminant analysis(SLDA) has resulted in removal of redundant variables, optimal linear combination of meaningful variables and formulation of classification rules. The plot in the first-to-second discriminant scores has shown that the three distinct territorial regions exist among porcelainsherds of Kyungki, Chunbuk-Chungnam, and Chunnam, with respective efficiencies of 20/30, 22/27 and 14/15. Similar regions have been found to exist among punchong porcelain and ceradonsherds of Kyungki, Chungnam and Chunbuk, with respective efficiencies of 7/9, 15/16 and 6/6. Classification has been further attempted by statistical isolinear multiple component analysis(SIMCA), using the sample set selected appropriately through SLDA as training set. For this purpose, all analytical data have been used. An agreement has generally been found between two methods, i.e., SLDA and SIMCA.

Introduction

As the trace element contents have been used to classify and identify archaeological specimens,[1,2] based on the assumption that their trace element patterns are correlated with the clay from which they originated,[3-5] it is possible that a similar study could establish the relationships between different clay sources and porcelainsherds and could recognize some pattern differences of trace elements to classify the sherds.

In PR(pattern recognition), two different situations can be considered according to whether the classes 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 then used to difine a classification rule, which could subsequently be applied to the classification of unknown samples.

In the previous works, PCA(principal component analysis) and SLDA(statistical linear discriminant analysis)[7] had been done to create some training set of porcelainsherds and potsherds, respectively. SLDA had further been applied in the development of classification rules for the unknown potsherds and in the recognition of relationships between different clay sources and potsherds.[8]

In this work, a study has been done in the defining of training set and in the development of classification rules for Korean ancient porcelainsherds by means of SLDA. The classification rules have been applied in the recognition of relationships between different clay sources and porcelainsherds. The results thus obtained have been compared with those by SIMCA[9] (statistical isolinear multiple component analysis) which was carried out by using the training set selected appropriately through SLDA.

Methods

Statistical Linear Discriminant Analysis(SLDA). The set of data on N samples with M variables, known to belong to two or more groups, can be represented as a set of N points in a M dimensional space. The aim of the discriminant function analysis is to arrive at a set of rules, which will classify samples into one of these groups with a minimal error. The discriminant function derived is given as a linear combination of the original variables and is of the form.[14]

$$f(x_{i1}, x_{i2}, \cdots, x_{ij}, \cdots, x_{iM}) = k_1 k_{i1} + k_2 x_{i2} + \cdots + k_j x_{ij} + \cdots + k_M x_{iM} \quad (1)$$

In vector notation, equation(1) can be written as $y_i = k \cdot x_i$ where k is the set of coefficients, x_i is the sample vector of individual i and Y_i is called the discriminant score(DS_i). The effect of very differing data ranges and variances of the various measured variables have been compensated by autoscaling the measured varibles to produce "features" with means of zero and variances of unity.[14]

The discriminant function is a linear combination of new variables and is now given in the form:

$$f(z_{i1}, z_{i2}, \cdots, z_{ij}, \cdots, z_{iM}) = v_1 z_{i1} + v_2 z_{i2} + \cdots + v_j z_{ij} + \cdots + v_M z_{iM} \quad (2)$$

In vector notation, equation(2) can be written as $Y_i = v \cdot z_i$, where V is the set of new coefficients and Z_i is the new sample vector of individual i. If there are K groups, each containing N_p(p=1,2,⋯, K) samples measured over M variables, the total number of samples is represented as $N = \sum_{p=1}^{k} N_p$.

The total dispersion matrix T for the new variables is given by,[14]

$$T = B + W \quad (3)$$

where B is the between-group matrix and W is the within-group matrix.

The projection of new variables Z_{ij} onto the vector described by coefficients V are given by $Y = V \cdot Z$. The between-group and the within-group dispersions for the projected points are given by $B_Y = V'BY$ and $W_Y = V'WV$, where B and W are obtained from original variables X_{ij}. If the ratio of the between-group dispersion to within-group dispersion of the projected points is defined as

$$L = (V'BV) / (V'WV) \quad (4)$$

L can be maximized according to Fisher's criterion as

$$\partial L / \partial V = 0$$

$$(BV/V'WV) - (V'BV/V'WV)(WV/V'WV) = 0 \quad (5)$$

Since L is defined as equation (4), equation (5) is given as

$$\left(\frac{BV}{V'WV}\right) - L \cdot \left(\frac{WV}{V'WV}\right) = 0 \text{ or} \quad (6)$$

$$BV = LWV$$

Multiplying both sides by W^{-1}, equation (6) is transformed as

$$W^{-1}BV = LV \quad (7)$$

From this equation, it is recognized that the coefficients V are given by eigen vector coefficients of matrix $W^{-1}B$ and L is the corresponding eigen value. Since L is difined as the ratio of the between-group dispersion to the within-group dispersion to obtain the maximum discrimination, the eigen vectors associated with the largest eigenvalue of the matrix $W^{-1}B$ should be used as the discriminant coefficients.

The number of eigenvalues extracted from the matrix $W^{-1}B$ will be equal to M or K-1(K is the number of groups) whichever is less. Hence M or K-1 discriminant functions, each with a different discriminant power, can be obtained.

Selection of Variables in SLDA. A pattern consisting of many parameters often contains a lot of noise, i.e., redundant parameters. These redundant parameters tend to obscure the difference between classes and therefore render the separation more difficult. The unnecessary parameters should be eliminated. To trace redundant variable several criteria are available.[14]

Criteria based on discriminant functions which are of the form as equation(4) give a larger importance to a variable when the absolute value of the corresponding weight coefficient is higher, provided that the variables have been standardized. A direct method is to determine the contribution percentage of each variable to the total distance D^2 in the discriminant space, which is the distance between the centroids of the group considered. The contribution percentage of variable j is given by $100 \times |v_j \delta_j| / D^2$, where v_j is the weight coefficient of the discriminant function for j th variable and

$$\delta_j = \frac{x_{p \cdot j} - x_{q \cdot j}}{\sigma_{\cdot \cdot j}} \quad (8)$$

$x_{p,j}$ and $x_{q,j}$ are the mean values of j th variable in group p and q, respectively.

Thus $D^2 = \sum_{j=1}^{M} |v_j \cdot \delta_j|$

Statistical Isolinear Multiple Component Analysis(SIMCA). The class q is difined by the parameters α, β, θ and ϵ in the principal component equation[9]:

$$y_{ik}^{(q)} = \alpha_i^{(q)} + \sum_{a=1}^{Aq} \beta_{ia}^{(q)} \theta_{ak}^{(q)} + \epsilon_{ik}^{(q)} \tag{9}$$

where y_{ik} is the feature of the i th constituent in the sample of the site k. A_q is the number of principal components. Before the model of equation(9) can be used, e.g., for the classification of a new object, values of the parameters $\alpha_i^{(q)}$, $\beta_{ia}^{(q)}$, $\theta_{qk}^{(q)}$ and σ_q^2 must be determined. The determination of $\beta_{ia}^{(q)}$ and $\theta_{ak}^{(q)}$ corresponds to a diagonalization of the matrices $Z^{(q)'} \cdot Z^{(q)}$, where $Z^{(q)}$ denotes the matrix obtained from the feature matrix of q th reference data set after subtracting the average of each variable $\alpha_i^{(q)}$. Hence, values of the parameters β_{ia} and θ_{ak} have been obtained for each class. The deviation $\epsilon_{ik}^{(q)}$ are then calculated by subtracting product terms of appropriate number A_q from the Z-value and variances σ_q^2 are then estimated from these deviation as $S_o^{(q)2}$:

$$S_o^{(q)2} = \sum_k^{nq} \sum_i^{M} (\epsilon_{ik}^{(q)2}) \,/\, [(n_q - A_q - 1)\,(M - A_q)] \tag{10}$$

where $i = 1,2,\ldots,$ M(M = number of variables), $a = 1,2,\ldots,$ A_q(A_q = number of the product terms in the model of eq. 9) and $k = 1,2,\ldots,$ n_q(n_q = number of objects in q th reference set). Thus, for the class q the model is calibrated by means of the data in the reference sets. The calibrated models can then be used to determine the classification of new objects as follows.

For the estimation of product terms A_q, the sum of the squares of the deviation Δ_A for each A-value for each object is calculated from each deviation ϵ_{ik}. The sum D_A is formed by adding the corresponding values Δ_A. These D_A-values are a measure of how well the model predicts the behavior of the reference-set for each value of A. By making F-tests on $(D_{A-1}-D_A)/(M-A_q)$ vs $D_A/[(n_q-A_q-1)(M-A_q)]$ one can determine whether the last product term (number A) is significant or not. The used critical F-value ($p = 0.05$) corresponds the number of degrees of freedom $(M-A_q)$ vs $(n_q-A_q-1)(M-A_q)$.

The observed features of the object p, say y_{ip}, have been fitted to the model of eq. (9) with the same numbers of the product terms and with the same values of the parameters $\alpha_i^{(q)}$ and $\beta_{ia}^{(q)}$ as were obtained in the calibration of the model, using eq. (11).

$$y_{ip} - \alpha_i^{(q)} = Z_{ip} = \sum_{a=1}^{Aq} C_{ap} \beta_{ia}^{(q)} + \epsilon_{ip}^{(q)} \tag{11}$$

For that purpose the parameter C_{ap} can be obtained by minimizing $\epsilon_{ip}^{(q)}$, using β_{ia} values obtained in the calibration of model. The variance $S_p^{(q)2}$ of deviation (ϵ_{ip}) thus obtained then indicates how well the object p fits class q.

$$S_p^{(q)2} = \sum_{i=1}^{M} (\epsilon_{ip}^{(q)})^2 / (M - A_q) \tag{12}$$

Experimental

Apparatus. Gamma-counting was done with a 75cc coaxial lithium-drifted germanium detector (ORTEC Model 8011-1619W) and a 4000-channel analyzer (ORTEC Model 7050). 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 area as described previously.[10]

Sampling and Pretreatments. Samples of porcelain-

Table 1. Sampling Sites and Their Corresponding Symbols for Porcelains and Clay Samples

Series number	Symbols	Number of samples	Sites	Items
1-19	△	19	Kwangju Kyungki-do	White porcelain
20-25	△(▽)	6(6)	Kwangju Kyungki-do	Punchong porcelain
26,27	△	2	Yongin Kyungki-do	White porcelain
28-30	△(▽)	3(3)	Yangju Kyungki-do	Ceradon
31-36	□(○)	6(6)	Puan Chullabuk-do	Ceradon
37-39	□	3	Puan Chullabuk-do	White porcelain
40-51	■(■)	12(11)	Kongju Chungchongnam-do	Punchong porcelain
52	■	1	Kongju Chungchongnam-do	White porcelain
53-57	■(■)	5(5)	Yongi Chunghongnam-do	Punchong porcelain
58-66	+	9	Haenam Chullanam-do	Ceradon
67-72	+	6	Wando-seabed Chullanam-do	Ceradon
	①	1	Yoju Kyungki-do	Clay
	②	1	Kangjin Chullanam-do	Clay
	③	1	Kangjin Chullanam-do	Clay
	④	1	Kangjin Chullanam-do	Clay
	⑤	1	Haenam Chullanam-do	Clay

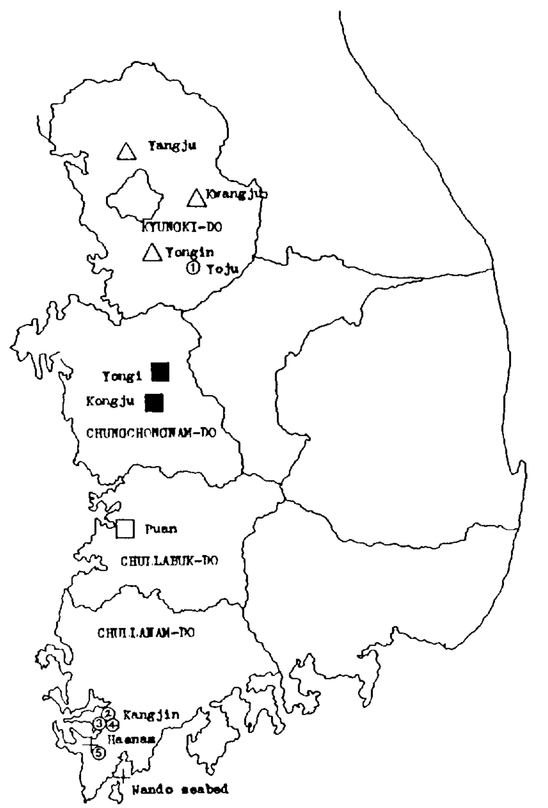

Figure 1. Map of Korea showing the sites at which samples were found. The sample symbols are defined in Table 1.

Table 2. Mean Values(ppm) of Elemental Contents in Porcelainsherds

Elements / Sites	Sm	Cu	Ga	K	La	Na	Ce	Lu	Th	Cr
Kyungki	2.65	84.3	22.3	1.76×10^4	25.9	6.36×10^3	63.4	0.272	17.7	37.1
Chunbuk-Chungnam	4.24	116	24.7	1.21×10^4	55.1	7.07×10^3	138	0.203	29.1	90.4
Chunnam	7.17	154	29.2	1.88×10^4	91.6	7.58×10^3	210	1.16	30.0	149
Total	4.19	111	24.6	1.58×10^4	50.5	6.88×10^3	122	0.431	24.7	80.3

Elements / Sites	Hf	Ba	Cs	Tb	Sc	Rb	Ta	Fe	Co	Eu
Kyungki	5.60	724	19.7	0.983	6.27	306	2.13	1.09×10^4	4.06	0.825
Chunbuk-Chungnam	10.4	789	15.5	1.09	13.7	226	2.66	1.55×10^4	6.87	1.18
Chunnam	17.7	891	12.3	1.26	214	254	2.22	3.20×10^4	9.88	2.62
Total	9.91	783	16.6	1.08	52.3	265	2.35	1.70×10^4	6.33	1.33

Table 3. Standard Deviations of Elemental Contents in Porcelainsherds

Elements / Sites	Sm	Cu	Ga	K	La	Na	Ce	Lu	Th	Cr
Kyungki	1.16	30.4	8.06	8.85×10^3	13.5	3.15×10^3	37.0	0.901	7.07	46.7
Chunbuk-Chungnam	0.831	66.7	6.18	3.12×10^3	13.9	4.11×10^3	44.9	0.0693	7.75	40.6
Chunnam	1.43	23.9	7.81	5.13×10^3	30.1	2.67×10^3	94.3	0.517	12.0	60.2
Total	2.02	53.1	7.69	7.02×10^3	30.7	3.45×10^3	78.9	0.727	10.4	63.4

Elements / Sites	Hf	Ba	Cs	Tb	Sc	Rb	Ta	Fe	Co	Eu
Kyungki	2.83	142	14.4	2.15	5.54	88.6	1.58	4.89×10^3	3.94	0.324
Chunbuk-Chungnam	3.83	284	17.8	0.434	4.17	63.7	5.04	8.68×10^3	3.77	0.502
Chunnam	7.76	706	4.33	1.01	741	78.5	1.58	1.38×10^4	2.38	0.619
Total	6.43	374	14.6	1.47	339	85.0	3.30	1.18×10^4	4.19	0.823

sherds from different sites in Korea were collected through museums. In Table 1 and Figure 1, the sites where the specimens were found are given together with the correspon-ding symbols. The whole samples were grouped into three classes, *i.e.*, Kyungki, Chunbuk-Chungnam and Chunnam, according to geographical similarity as shown in Table 1. The samples of punchong and ceradon sherds were further grouped into three subclasses Kyungki, Chungnam and Chunbuk according to sites, using the symbols in paren-theses as shown in Table 1. The sherds 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 sherds, *i.e.*, the surface and glaze was eliminated. An accurate amount of each sample was weighed and sealed in 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 known amounts of Au and Co as monostandards.[11] Use of two nuclides with different nuclear properties facilitates the evaluation of effective activation cross section of all nuclides involved in activation for a given condition[12].

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, the surface of each silica vial was cleaned with dilute nitric acid and the sealed vial was placed on a given geometry of detector(the background of the vial was negligible). The same vial was re-counted 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 shown in the procedure describ-ed in the previous paper[11-13] by using flux indices at the ir-radiation conditions, nuclear data given in references and counting efficiency curves at given geometries.

Results and Discussion

Twenty elements(Na, K, Sc, Cr, Fe, Co, Cu, Ga, Rb, Cs, Ba, La, Ce, Sm, Eu, Tb, Lu, Hf, Ta and Th), which were analyzed by neutron activation analysis, have been used in the present PR study for the classification of porcelainsherds collected from various sites as shown in Table 1 and Figure 1. The means and standard deviation of the variables. *i.e.*, elemental contents, have been calculated for each group and overall samples and are given in Table 2 and 3, respectively.

The total within-group matrix W and between-group matrix B in equation (3) have been generated from original data set as well as the data given in Table 2 and 3. Charac-

Table 4. Data for the Selection of Variables

Elements / Sites	Sm	Cu	Ga	K	La	Na	Ce	Lu	Th	Cr
$V_1^a\delta^b_{AB}$	0.32	0.14	0.041	0.11	0.23	0.019	0.17	0.026	0.12	0.000
C^c (%)	16	6.6	2.0	5.5	11	0.94	8.1	1.3	6.0	0.00
$V_1^a\delta^b_{BC}$	0.60	0.16	0.079	0.14	0.28	0.014	0.16	0.36	0.021	0.000
C (%)	16	4.3	2.1	3.7	7.6	0.38	4.3	9.6	0.55	0.00

Elements / Sites	Hf	Ba	Cs	Tb	Sc	Rb	Ta	Fe	Co	Eu
$V_1\delta_{AB}$	0.30	0.006	0.018	0.005	0.002	0.17	0.010	0.082	0.067	0.24
C (%)	15	0.27	0.86	0.22	0.073	8.1	0.47	4.0	3.2	11
$V_1\delta_{BC}$	0.47	0.009	0.014	0.008	0.040	0.059	0.008	0.29	0.072	0.94
C (%)	13	0.23	0.37	0.21	1.1	1.6	0.22	7.9	1.9	25

[a] The coefficients of discriminant function corresponding to eigenvalue L_1. [b] $\delta_{AB} = \left(\frac{m_{A,j} - m_{B,j}}{\sigma_{\cdot\cdot j}}\right)$ $m_{A,j}$, $m_{B,j}$; the mean values of the jth variable in group A and B. $\sigma_{\cdot\cdot j}$; the overall standard deviation of the jth variable. A, B and C are denoted to Kyungki, Chunbuk-Chungnam and Chunnam, respectively. [c] Contribution percentage $\left(=\frac{|V_j\delta_{AB}|}{D^2}\times 100,\ D^2 = \sum_{j=1}^{M} V_j\delta_{AB}\right)$

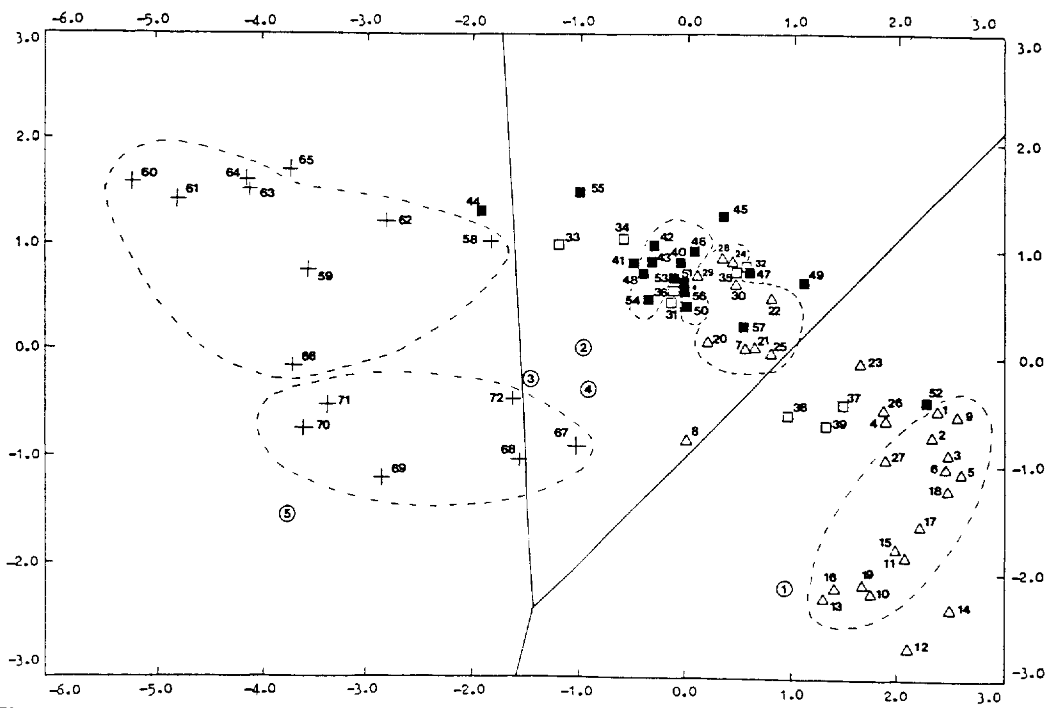

Figure 2. Plot and territorial map of discriminant score 1 versus discriminant score 2 for the Kyungki/Chunbuk-Chungnam/Chunnam porcelainsherds. For the symbols, see Table 1.

teristic roots of $W^{-1}B$ matrix of equation (7) have been found. The discriminant function corresponding to the largest eigen value L was selected. The contribution percentage of each element to the total distance D^2 in the discriminant space has been estimated, using eigen vector coefficient v_j, *i.e.*, the weighting factor corresponding to each element in equation (2) along with fractional distance δ_i between classes.

Data for the selection of variables are given in Table 4. The contribution percentage of each element to the distance between group A and C is not given in Table 4 because the two groups are not seriously overlapped. From the results on Table 4, the classification between groups has been found to be mainly attributed to 11 elements such as Sm, Cu, K, La, Ce, Lu, Th, Hf, Rb, Fe and Eu.

Using the data of the selected 11 elements, $W^{-1}B$ matrix (11 × 11) has been generated again. Since a three-fold classification problem is involved, two discriminant functions can be derived and the second discriminant function corresponding to the second largest eigen value L_2 has been computed similarly as described above. The two discriminant scores for individual i, corresponding to eigen values L_1 and L_2, have been generated for Kyungki, Chunbuk-Chungnam and chunnam porcelainsherds as follows:[7,8,14]

Table 5. Prediction Results for the Kyungki, Chunbuk-Chungnam and Chunnam Porcelainsherds

A priori group membership	Number of samples	A posteriori(predicted) group membership Kyungki	Chunbuk-Chungnam	Chunnam
Kyungki	30	20(28%)	4(5.6%)	0(0.0%)
Chunbuk-Chungnam	27	10(14%)	22(31%)	1(1.4%)
Chunnam	15	0(0.0%)	1(1.4%)	14(19%)

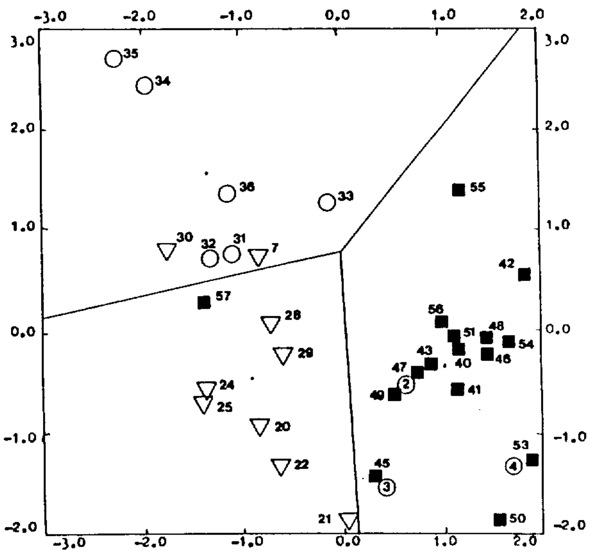

Figure 3. Plot and territorial map of discriminant score 1 versus discriminant score 2 for the subgrouping of Kyungki/Chunbuk/Chungnam Punchong and Ceradonsherds. For the symbols, see those in parentheses in Table 1.

$L_1 = 5.97$

$DS_{1,i} =$

$$-2.66\times10^{-1}X_{Sm,i}-2.71\times10^{-3}X_{Cu,i}-2.70\times10^{-5}X_{K,i}$$
$$-9.60\times10^{-3}X_{La,i}-1.57\times10^{-3}X_{Ce,i}-4.90\times10^{-1}X_{Lu,i}$$
$$+4.92\times10^{-3}X_{Th,i}-6.30\times10^{-2}X_{Hf,i}+3.07\times10^{-3}X_{Rb,i}$$
$$-1.24\times10^{-5}X_{Fe,i}-4.99\times10^{-1}X_{Eu,i}+3.29$$

$L_2 = 2.33$

$DS_{2,i} =$

$$-2.66\times10^{-1}X_{Sm,i}+2.71\times10^{-3}X_{Cu,i}-6.09\times10^{-6}X_{K,i}$$
$$+1.12\times10^{-2}X_{La,i}+3.26\times10^{-3}X_{Ce,i}+1.05\times10^{-1}X_{Lu,i}$$
$$+2.81\times10^{-2}X_{Th,i}+4.00\times10^{-2}X_{Hf,i}-4.74\times10^{-3}X_{Rb,i}$$
$$-3.56\times10^{-6}X_{Fe,i}+1.59\times10^{-5}X_{Eu,i}+0.995$$

By the procedure adopted previously, both of discriminant functions are found to be statistically significant. The hypothesis is similarly accepted that the differentiation among the groups on the basis of both discriminant functions is significant and not due to chance or sampling errors.

Figure 2 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 distance between each pair of group centroids.

Sample i has been classified according to its position on the discriminant axis as compared to the position of centroids $\overline{DS}_p$ and $\overline{DS}_q$ of groups p and q, respectively. In the present work, this classification rule can be described as follows: assign sample i to Kyungki group if $A_c \le B_c$ and $A_c < C_c$; Chunbuk-Chungnam group if $B_c \le C_c$ and $B_c < A_c$; Chunnam group if $C_c \le A_c$ and $C_c < B_c$, when

$$A_c = [(DS_{1,i}-\overline{DS}_{1,\text{ Kyungki}})^2 + (DS_{2,i}-\overline{DS}_{2,\text{ Kyungki}})^2]^{1/2}$$
$$B_c = [(DS_{1,i}-\overline{DS}_{1,\text{ Chunbuk-Chungnam}})^2 + (DS_{2,i}-\overline{DS}_{2,\text{ Chunbuk-Chungnam}})^2]^{1/2}$$
$$C_c = [(DS_{1,i}-\overline{DS}_{1,\text{ Chunnam}})^2 + (DS_{2,i}-\overline{DS}_{2,\text{ Chunnam}})^2]^{1/2}$$

This classification corresponds to Mahalonobis distance classifier discussed by Coomans and Massart.[14]

The above classification procedure has been applied to all porcelainsherds which have been used as training set in this study and the number of correctly classified individuals has been determined. Written as percentage, this expresses the efficiency of classification procedure. The classification results are shown in Table 5. It should be noted that when this method is used, 56 samples of 72 porcelainsherds have been correctly classified.

The above classification procedure has been applied to classify a set of samples consisting of punchong porcelain and ceradonsherds into three subgroups as shown in Table 1, *i.e.*, Kyungki, Chunbuk and Chungnam. For this purpose, elements have been selected as described above. The results showed that differentiation between subgroups was attributed mainly to 9 elements, namely, La, Na, Cr, Hf, Ba, Sc, Rb, Fe and Co. The discriminant scores for individual i which correspond to eigen values L_1 and L_2 generated. The results are as follows:

$L_1 = 7.48$

$$DS_{1,i} = 1.91\times10^{-2}X_{La,i}+2.16\times10^{-4}X_{Na,i}-6.04\times10^{-3}X_{Cr,i}$$
$$-7.89\times10^{-2}X_{Hf,i}+2.25\times10^{-3}X_{Ba,i}-2.08\times10^{-1}X_{Sc,i}$$
$$-4.23\times10^{-3}X_{Rb,i}-3.26\times10^{-6}X_{Fe,i}-8.46\times10^{-2}X_{Co,i}$$
$$-5.67$$

$L_2 = 3.07$

$$DS_{2,i} = 2.50\times10^{-2}X_{La,i}-1.28\times10^{-4}X_{Na,i}+1.16\times10^{-2}X_{Cr,i}$$
$$+1.02\times10^{-1}X_{Hf,i}+2.13\times10^{-3}X_{Ba,i}+1.42\times10^{-1}X_{Sc,i}$$
$$+2.18\times10^{-3}X_{Rb,i}-4.87\times10^{-5}X_{Fe,i}-1.76\times10^{-1}X_{Co,i}$$
$$-4.74$$

Table 6. Prediction Results for the Kyungki, Chunbuk and Chungnam Punchong Porcelain and Ceradonsherds.

A priori group membership	Number of samples	A posteriori(predicted) group membership Kyungki	Chunbuk	Chungnam
Kyungki	9	7(23%)	0(0.0%)	1(3.2%)
Chunbuk	6	2(6.5%)	6(19%)	0(0.0%)
Chungnam	16	0(0.0%)	0(0.0%)	15(48%)

Table 7. Assignment of Samples for Training Set and Test Set. The Numbers in Parentheses are Class Numbers

Sample no.	Symbols defined for SLDA	Class given for SIMCA	Assignment calculated	Distance to nearst class, $S_p^{(q)}$	Distance to related class, $S_p^{(q)}$
	Training set for class 1				
1		1	1	0.3607 (1)	4.928 (2)
2		1	1	0.3701 (1)	4.549 (2)
3		1	1	0.4243 (1)	4.045 (2)
5		1	1	0.4018 (1)	4.840 (2)
6		1	1	0.3642 (1)	4.982 (2)
9		1	1	0.3213 (1)	4.680 (2)
10	△	1	1	0.3077 (1)	4.938 (2)
11		1	1	0.4949 (1)	4.822 (2)
13		1	1	0.0936 (1)	5.972 (2)
15		1	1	0.4548 (1)	5.067 (2)
16		1	1	0.3413 (1)	5.593 (2)
17		1	1	0.4890 (1)	5.254 (2)
18		1	1	0.5256 (1)	4.423 (2)
19		1	1	0.5386 (1)	4.624 (2)
27		1	1	0.2024 (1)	4.197 (2)
	Training set for class 2				
20		2	2	0.7575 (2)	7.223 (1)
21		2	2	0.6059 (2)	7.433 (1)
22		2	2	0.4441 (2)	7.192 (1)
24	△	2	2	0.5763 (2)	5.591 (1)
25		2	2	0.6424 (2)	5.862 (1)
28		2	2	0.5187 (2)	5.918 (1)
29		2	2	0.4518 (2)	9.458 (1)
30		2	2	0.5658 (2)	5.208 (1)
	Training set for class 3				
40		3	3	0.3404 (3)	
42		3	3	0.3318 (3)	
43		3	3	0.3515 (3)	
46		3	3	0.2247 (3)	
48		3	3	0.2756 (3)	
50	■	3	3	0.1215 (3)	
51		3	3	0.3645 (3)	
53		3	3	0.3830 (3)	
54		3	3	0.3420 (3)	
56		3	3	0.1065 (3)	
	Training set for class 4				
58		4	4	0.3545 (4)	10.78 (5)
59		4	4	0.3430 (4)	14.91 (5)
60		4	4	0.3540 (4)	3.986 (5)
61		4	4	0.3426 (4)	8.836 (5)
62	+	4	4	0.3106 (4)	4.227 (5)
63		4	4	0.1051 (4)	4.989 (5)
64		4	4	0.3810 (4)	12.20 (5)
66		4	4	0.1166 (4)	5.126 (5)
	Training set for class 5				
67		5	5	0.3973 (5)	1.752 (4)
68		5	5	0.5776 (5)	1.490 (4)
69	+	5	5	0.5948 (5)	2.134 (4)
70		5	5	0.3011 (5)	1.753 (4)
71		5	5	0.5217 (5)	1.584 (4)
72		5	5	0.5361 (5)	1.352 (4)
	Test set				
4	△	1	outlier	3.696 (1)	
7	△	1,2	outlier	1.448 (2)	5.522 (1)
8	△	1,2	outlier	6.602 (1)	14.11 (2)
12	△	1	outlier	2.124 (1)	
14	△	1	outlier	0.9411 (1)	
23	△	2,1	outlier	2.400 (2)	4.317 (1)
26	△	1	outlier	1.165 (1)	
31	□	3,2	outlier	0.7863 (4)	1.167 (3), 1.771 (2)
32	□	2,3	outlier	1.035 (4)	2.055(2), 1.843(3)
33	□	3	4	0.5322 (4)	1.538(3)
34	□	3	4	0.7220 (4)	1.890 (3)
35	□	2,3	2	0.9348 (4)	0.9885 (2), 1.879 (3)
36	□	3	4	0.7048 (4)	1.027 (3)
37	□	1,3	outlier	4.044 (1)	14.28 (3)
38	□	1,3	outlier	2.941 (4)	4.210 (1), 8.852 (3)
39	□	1,3	outlier	3.045 (4)	3.303 (1), 9.347 (3)
41	■	3	3	0.7290 (3)	
44	■	4,3	outlier	2.037 (4)	3.032 (3)
45	■	3	outlier	1.167 (4)	1.715 (3)
47	■	2,3	outlier	1.043 (4)	1.444 (2), 1.062 (3)
49	■	3	outlier	1.326 (4)	1.807 (3)
52	■	1,3	outlier	1.914 (4)	3.324 (1), 4.578 (3)
55	■	3	outlier	7.168 (4)	14.75 (3)
57	■	2,3	outlier	0.9944 (4)	1.671 (2), 2.089 (3)
65	+	4	4	0.6481 (4)	
Clay ①		1		2.839 (1)	
②		3		1.562 (4)	2.443 (3)
③		3		1.221 (4)	4.226 (3)
④		3		1.550 (4)	3.022 (3)
⑤		5,4		2.233 (4)	2.489 (5)

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

Figure 3 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 similar classification rule as above can be descriptive. The classification results obtained as described above are shown in Table 6. As the results, 28 samples in 31 sherds have properly classified. Five clay samples, which are supposed to have served as the source material of porcelainsherds have been included in Figure 1 to differentiate them into groups. Figure 2 shows that clay①is allocated to Kyungki group, clay②-④to Chunbuk-Chungnam, and clay⑤to Chunnam. All these results are in accord with the geographical prediction based on excavated sites of porcelainsherds and sampling sites of clay. Figure 3 shows that clay②-④are allocated to Chungnam subgroup even though they have been sampled in Chunnam. However, this contradiction could be possible by considering the vicinity of two geographical sites.

The five training set, *i.e.*, the sample set in dotted areas in Figure 2, have been chosen for the SIMCA on the basis of geographical difference and the spread of sample sites in the two dimensional plots such as Figure 2 and 3. The training set thus defined as well as other samples which have been chosen as test set are given in Table 7.

Values of the parameters, *i.e.*, $\alpha_i^{(q)}$, $\beta_{ia}^{(q)}$, $\theta_{ak}^{(q)}$ and σ_q^2 for $q = 1, \ldots, 5$, in equations (9) and (10) have been determined from the data of training set and are given in Table 8(a) and 8(b). For the estimation of the product number of similarity model, D_A values were calculated for each A value from the deviation ϵ_{ik} obtained by fitting. The necessary numbers of A values were found by means of F-tests and are given in Table 9 along with critical F values.

The variances of deviation ϵ_{ip}, *i.e.*, $S_p^{(q)2}$ in equation (12), were calculated for the object p in both training and test set. An F-test has been made on the value $F = S_p^{(q)2} \cdot \frac{n_q}{(n_q - A_q - 1)} / S_0^{(q)2}$. In this case, $(M - Aq)$ vs $(n_q - A_q - 1)(M - A_q)$ has been used as the critical F-value, so as to determine whether the object p belongs to any class q or an outlier.[9]

The distances $S_p^{(q)}$ which correspond to orthogonal distance between objects p and class q are given in Table 7. This table shows that whole samples in the training set which have been selected on the basis of SLDA results have properly assigned by SIMCA. Nineteen samples in 25 test samples have been found to be outliers from any groups, which would be attributable to much restriction on modeling of each group for SIMCA. 5 clay samples have been found to be outliers from any group but found to be assigned properly on the basis of the distance $S_p^{(q)}$ by considering the geographical vicinity between sampling sites and assigned sites for clay.

Table 9. Standard Deviations and Critical F-values of Training Set for Class q

Class (q)	q=1	q=2	q=3	q=4	q=5
Standard deviation, $S_0^{(q)}$	0.5797	0.8180	0.5601	0.5008	0.7442
Critical F-value (A_q)	2.28(7)	2.05(3)	2.26(6)	2.13(4)	2.03(2)

Table 8(a). Parameter Values $\beta_{ia}^{(q)}$ for Models of SIMCA. Class Numbering (q) Same as in Table 7

β-Values Normalized so that $\sum_{i=1}^{20} \beta_{ia}^{(q)2} = 1$

Elements	$\alpha_i^{(q)}$	Class 1(q=1)							Class 2(q=2)			Class 3(q=3)						Class 4(q=4)				Class 5(q=5)	
		$\beta_{1a}^{(q)}$	$\beta_{2a}^{(q)}$	$\beta_{3a}^{(q)}$	$\beta_{4a}^{(q)}$	$\beta_{5a}^{(q)}$	$\beta_{6a}^{(q)}$	$\beta_{7a}^{(q)}$	$\beta_{1a}^{(q)}$	$\beta_{2a}^{(q)}$	$\beta_{3a}^{(q)}$	$\beta_{1a}^{(q)}$	$\beta_{2a}^{(q)}$	$\beta_{3a}^{(q)}$	$\beta_{4a}^{(q)}$	$\beta_{5a}^{(q)}$	$\beta_{6a}^{(q)}$	$\beta_{1a}^{(q)}$	$\beta_{2a}^{(q)}$	$\beta_{3a}^{(q)}$	$\beta_{4a}^{(q)}$	$\beta_{1a}^{(q)}$	$\beta_{2a}^{(q)}$
Sm	0	0.2763	0.0137	0.1527	0.1699	0.2984	0.2936	0.2239	0.1092	-0.2581	0.04373	-0.2237	0.2710	0.00884	0.1369	0.07268	-0.5200	0.2029	-0.3135	0.05992	-0.2057	0.00567	0.3244
Cu	0	-0.05349	0.2558	-0.4417	-0.2312	-0.02047	-0.1078	0.3619	-0.2372	-0.2424	0.2408	-0.09289	-0.1133	-0.5106	0.1257	0.1896	0.02655	0.2136	0.2417	-0.1546	0.02814	0.000	0.000
Ga	0	0.02128	-0.3117	-0.3075	0.1104	0.3236	-0.1550	0.3323	0.1825	0.2499	-0.3043	0.1251	0.02103	-0.01906	-0.3710	0.5953	0.2378	0.1966	-0.0193	0.4324	0.1320	0.08234	0.1258
K	0	0.1125	0.4223	0.1145	0.07021	-0.1474	-0.06046	0.1433	0.05592	0.2397	-0.1862	0.2231	0.01573	-0.2665	-0.3435	-0.06975	-0.1298	0.2333	0.1327	0.3136	0.2481	0.2720	-0.2114
La	0	0.3358	-0.1069	-0.01353	-0.1528	0.2673	0.03140	0.1582	0.03980	-0.2859	-0.1131	-0.1459	0.3111	0.07155	-0.1597	0.3092	-0.4691	0.2837	0.1557	0.1300	0.04050	0.2217	0.02815
Na	0	0.06034	0.3987	-0.2330	-0.06732	-0.1367	-0.1162	0.09844	-0.3422	-0.2127	-0.02394	-0.06085	-0.2440	-0.4437	0.08913	0.2135	0.03308	0.2199	0.2474	-0.1945	0.07825	0.2989	0.06074
Ce	0	0.2484	-0.2626	0.07585	-0.08352	-0.08691	0.3715	-0.1530	0.00548	-0.0571	-0.4603	-0.01331	0.3023	0.1178	-0.2658	-0.2479	0.09915	0.07635	0.4133	0.2449	-0.02290	0.1555	0.2024
Lu	0	0.3096	-0.02876	-0.2561	0.2172	0.07397	-0.02610	-0.4679	-0.04513	-0.1117	-0.4513	0.3040	-0.1067	0.2175	0.1199	0.05993	-0.2814	0.1331	0.1420	-0.02514	-0.6923	0.2680	0.08807
Th	0	0.2452	-0.03684	-0.07157	-0.4479	-0.3209	0.03249	-0.03317	0.3700	0.02495	0.07983	-0.01046	0.495	-0.1356	0.1527	0.04810	0.1987	0.2527	-0.2291	0.1069	-0.1639	0.2999	0.1453
Cr	0	0.1064	-0.2987	0.05556	0.06536	-0.04731	-0.4964	-0.1681	0.1547	-0.3590	-0.00245	0.2431	0.2358	-0.2476	0.02369	-0.3394	0.09560	0.2823	0.06649	-0.1863	0.1349	0.2988	0.07021
Hf	0	-0.04577	-0.3262	0.1869	-0.3823	-0.02085	-0.02013	0.4010	-0.2505	0.1615	-0.2929	0.3221	0.02521	0.1165	0.3050	0.00824	-0.1815	0.2268	-0.1764	0.2616	0.3329	0.2684	-0.2509
Ba	0	-0.1030	-0.1270	-0.2066	0.4437	-0.3340	-0.2059	0.1106	0.08106	0.01003	-0.01117	-0.07375	0.03628	0.4115	0.2896	0.00483	0.3587	-0.09577	-0.1682	0.3872	-0.1431	0.2620	0.1524
Ca	0	0.2994	-0.09880	-0.07130	0.3073	-0.02975	-0.09772	0.3026	0.3622	0.0001	-0.1126	0.1147	0.3238	0.1770	-0.1709	0.3504	0.2018	0.2172	-0.3044	0.04588	-0.2559	0.1437	0.2522
Tb	0	0.2924	-0.07937	-0.2079	-0.1731	0.2273	-0.2813	-0.1421	-0.09887	-0.2178	-0.3202	-0.2478	0.2945	-0.1723	0.1926	-0.04002	-0.1176	0.1400	-0.2200	-0.4073	0.2353	0.1211	-0.2810
Sc	0	0.02987	-0.2914	0.1543	0.1868	-0.4768	0.05826	0.2357	0.2386	-0.3551	-0.03555	0.2364	0.2751	-0.1218	-0.2479	-0.2142	0.00872	0.3068	0.1124	0.01828	-0.09270	0.3098	0.09311
Rb	0	0.3461	0.01336	-0.04220	-0.04274	-0.2875	-0.1132	0.03744	0.2709	-0.2577	0.02376	0.3103	0.2092	-0.1059	0.2266	0.1304	0.05120	0.2726	-0.2218	0.00500	0.1097	-0.1228	0.4696
Ta	0	0.3157	0.00172	-0.1185	-0.1695	-0.2720	0.05501	-0.07341	-0.1030	-0.2210	0.3118	0.3015	-0.01266	0.01859	0.3587	0.2648	-0.02440	0.1229	-0.4129	-0.1579	0.09990	-0.1870	0.3917
Fe	0	0.2426	0.2034	0.3786	0.1386	-0.03247	-0.04160	0.06269	0.3760	0.1104	0.08079	0.3856	0.00271	0.04405	-0.04371	0.04391	-0.1498	0.2847	0.05832	0.1110	-0.1125	0.2764	0.1495
Co	0	0.05712	0.1100	0.4776	-0.1240	0.1132	-0.5572	-0.00280	0.3165	0.1646	0.1314	0.3146	0.04028	-0.1853	0.1028	-0.1042	0.00363	0.2732	0.00108	-0.2502	-0.1961	0.2801	-0.2077
Eu	0	0.3035	0.2257	0.05349	0.2146	0.1157	0.1046	0.1742	0.1449	-0.3581	-0.2315	-0.1568	0.3281	-0.1357	0.2652	0.07457	0.2341	0.2338	0.2356	-0.1980	0.1069	0.1692	0.2794

Table 8(b). Parameter Values for θ_{ak}, Object Numbering(k) and Class Numbering(q) Same as in Table 7

	Class 1(q=1)								Class 2(q=2)				Class 3(q=3)							Class 4(q=4)					Class 5(q=5)	
k	$\theta_{1k}^{(q)}$	$\theta_{2k}^{(q)}$	$\theta_{3k}^{(q)}$	$\theta_{4k}^{(q)}$	$\theta_{5k}^{(q)}$	$\theta_{6k}^{(q)}$	$\theta_{7k}^{(q)}$	k	$\theta_{1k}^{(q)}$	$\theta_{2k}^{(q)}$	$\theta_{3k}^{(q)}$	k	$\theta_{1k}^{(q)}$	$\theta_{2k}^{(q)}$	$\theta_{3k}^{(q)}$	$\theta_{4k}^{(q)}$	$\theta_{5k}^{(q)}$	$\theta_{6k}^{(q)}$	k	$\theta_{1k}^{(q)}$	$\theta_{2k}^{(q)}$	$\theta_{3k}^{(q)}$	$\theta_{4k}^{(q)}$	k	$\theta_{1k}^{(q)}$	$\theta_{2k}^{(q)}$
1	-2.993	-0.1762	-3.419	-0.3943	0.6342	0.1460	0.7075	20	1.795	-0.8866	-1.251	40	-1.702	1.164	0.3102	-0.4968	1.303	0.7534	58	-5.232	-0.2964	-0.5597	0.3258	67	-2.319	-2.447
2	-2.228	-1.539	-1.176	1.256	0.5143	1.013	0.01260	21	1.687	-1.286	1.850	42	-1.495	-1.106	-3.009	-2.019	0.7260	-0.1770	59	-2.328	-0.8957	2.740	-0.6316	68	-1.375	0.9246
3	1.114	-3.102	-0.2458	-2.478	-1.549	0.1265	0.8104	22	0.9347	-2.551	2.031	43	-1.969	1.199	0.1925	1.551	-1.781	-1.022	60	4.306	-0.1921	1.347	-1.414	69	-2.192	2.660
5	-1.962	-2.082	0.4989	1.495	0.1062	0.3007	-0.6523	24	0.6199	3.796	0.9654	46	-2.393	-2.557	1.443	-0.2113	-0.4322	1.558	61	2.516	2.307	-1.443	0.0332	70	5.290	1.050
6	1.617	-4.451	1.735	1.534	-1.103	-0.1902	0.1583	25	2.724	1.841	-2.089	48	-2.629	2.638	2.277	-0.6610	0.6854	-0.8069	62	-2.362	0.6261	-0.9197	-0.6895	71	2.447	-1.874
9	-2.263	-1.125	-0.5202	0.1241	1.324	-1.699	-0.5549	28	-3.914	0.8501	-0.4907	50	4.454	2.674	0.1091	-2.116	-0.9964	0.3982	63	1.480	0.8632	1.224	2.651	72	-1.847	-0.3174
10	0.2406	2.749	0.2263	0.4374	-0.6984	1.059	-0.7904	29	-1.520	-2.493	-2.419	51	3.024	-0.0954	0.8864	2.119	0.7115	0.9777	64	-0.1795	2.049	-0.8147	-0.6056			
11	1.124	1.268	0.4327	-1.797	-0.0621	-1.404	0.6637	30	-2.329	0.7227	1.409	53	-0.5749	-0.4857	-1.855	0.6420	-1.838	0.3774	66	1.802	-4.468	-1.581	0.3204			
13	7.272	0.4454	-2.296	0.6390	0.4587	-0.3183	-0.7513					54	1.018	0.5338	-1.945	1.915	1.506	-0.5865								
15	-1.237	1.697	1.261	0.5689	-0.1222	-1.794	-0.3210					56	2.258	-3.959	1.593	-0.7168	0.1151	-1.463								
16	0.9801	1.833	0.5885	1.346	0.9636	0.3562	1.953																			
17	-2.009	2.274	0.1362	0.1269	-1.291	-0.0738	-0.4751																			
18	-0.5780	0.8443	-0.4598	-1.254	-1.925	0.6498	-0.6531																			
19	0.2844	2.018	1.430	0.6954	-0.1983	0.7666	0.5899																			
27	0.6435	-0.6456	1.808	-2.301	2.956	1.061	-0.6978																			
S.D	2.539	2.145	1.455	1.384	1.249	0.9546	0.7996		2.324	2.211	1.792		2.519	2.131	1.707	1.519	1.212	0.9697		3.133	2.123	1.569	1.223		3.145	1.930
Range	7.272	2.749	1.808	1.534	2.956	1.061	1.953		2.724	3.796	2.031		4.454	2.674	2.277	2.119	1.506	1.558		4.306	2.307	2.740	2.651		5.290	2.660
	-2.993	-4.451	-3.419	-2.478	-1.925	-1.794	-0.7513		-3.914	-2.551	-2.419		-2.629	-3.959	-3.009	-2.116	-1.838	-1.463		-5.232	-4.468	-1.581	-1.414		-2.319	-2.447

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Synthesis of new Hydantoin-3-Acetic acid Derivatives

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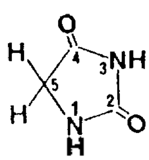
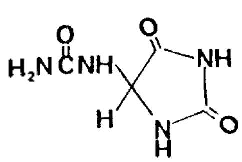
Through the Bucherer-Berg method, new 5-alkylthiomethyl or 5-alkylsulfonylmethylhydantoins were prepared. The reaction of ethyl chloroacetate with these compounds gave 3-acetate and the subsequent hydrolysis with dilute sodium hydroxide resulted in 3-hydantoinacetic acid derivatives. These products are expected to exhibit anti-inflammatory and analgestic activities.

Introduction

Hydantoin (2,4-imidazolidinedione, glycolurea) was first discovered by Bayer in 1861 as a hydrogenation product of allantoin and its derivatives are important intermediates in the synthesis of several amino acids and also used as anticonvulsants or antibacterials.[1-7] In the course of our studies on



hydantoin



allantoin

the development of new pharmaceutically active substances, several hydantoin derivatives were prepared. Of these we report the synthesis of 3-hydantoinacetic acid derivatives with alkylthio or alkylsulfonylmethyl group at the 5-position of hydantoin ring, which are known to exhibit anti-inflammatory and analgestic activities.[8,9]

Most of hydantoin derivatives were prepared in good yield through the Bucherer-Berg synthesis, i.e. the reaction of corresponding ketones with 2 mol. equivalent of potassium cyanide and 4 mol. equivalent of ammonium carbonate in 60% aqueous alcohol at 65°C.[5,10-14] Kwon and his co-workers synthesized several 5-aryl-5-alkylthiomethyl-hydantoins and their anti-inflammatory properties were determined in the rat paw oedema test.

Recently they reported the preparation of twenty 5,5-disubstituted 3-hydantoinacetic acid derivatives for developing new anti-inflammatory and analgestic agents.[9] These compounds were screened for the above effects and as a result five of them, e.g. 5-phenyl-5-propylthiomethyl hydantoin-3-acetate showed a significant analgestic activity. Therefore we introduced some other alkylthiomethyl group on the 5-position of hydantoin ring and also chloroacetone, in stead of phenacyl chloride, was utilized to modify the other substituent on that position. We expect the better anti-inflammatory or analgestic effects for this kind of derivatives and the results of screening will be reported later in the separate paper.

Results and Discussions

By the reaction of phenacyl chloride or chloroacetone with alkyl(or aryl)mercaptan, phenyl(or methyl) alkyl(or aryl) thiomethyl ketones were prepared and they were converted to 5-phenyl(or methyl)-5-alkyl(or aryl)thiomethylhydantoins by Bucherer-Berg synthesis in good yields. The reaction of ethyl chloroacetate with these compounds gave the corres-