

Yoshihiro Hiraoka,¹ M.S.

A Possible Approach to Soil Discrimination Using X-ray Fluorescence Analysis

REFERENCE: Hiraoka, Y., "A Possible Approach to Soil Discrimination Using X-ray Fluorescence Analysis," *Journal of Forensic Sciences*, JFSCA, Vol. 39, No. 6, November 1994, pp. 1381-1392.

ABSTRACT: Soil samples collected from 110 different sites in the Kyoto district, Japan, were analyzed quantitatively using X-ray fluorescence spectroscopy to predict unknown soil origins. More than 250 mg soil samples, ground to -100 + 200 mesh and pressed, were analyzed for Si, K, Ca, Ti, Fe, Rb and Sr with good reproducibility. Analytical data were normalized to a standard rock sample (JG-1) and were subjected to multivariate analysis. Especially trace elements, such as Sr and Rb, as well as K and Fe were available to characterize soil samples, and these soils were classified into nine types that show good agreement with geological features. Probabilities of correct identity by comparing unknown soils with control data sets were about 71%, according to the systematic discrimination that was derived from multivariate analysis and a geochemical survey map of soils.

KEYWORDS: criminalistics, soil discrimination, X-ray fluorescence analysis, multivariate analysis, geochemical survey map of soils, forensic investigation

Soil constitutes important physical evidence and may be encountered in a wide variety of criminal investigations. It is useful in linking the suspect or victim to a location. Several authors have demonstrated how to predict origins of unknown soils by means of soil color [1], particle size [2], decomposed organic materials [3], enzymatic characterization [4], clay minerals [5] and opal phytoliths [6].

In this paper, the measurement of various soil samples from the Kyoto district, Japan, based on the X-ray fluorescence analysis (XRF) and multivariate analysis of the resulting analytical data [7] are reported as a test case. In the first instance, the precision and reproducibility of the instrument employed are assessed, using different soil samples originating from the same locality; then the sensitivity limit of the X-ray fluorescence spectrometer used in this study is investigated. Secondly, the available elements for soil discrimination are chosen by comparing the chemical features of soils with their localities. Thirdly, the analytical results of as many as 850 known soils are classified by using multivariate analysis. Then, the geochemical survey map of soils in the Kyoto district is illustrated precisely. Finally, the automated system for soil discrimination is contrived and the blind test is applied to this system.

Thus, this paper proposes a possible approach to the prediction of unknown soil origins by comparing the analytical results obtained with relatively large number of control data sets using a personal computer.

Received for publication 27 July 1993; revised manuscript received 23 Nov. 1993 and 30 March 1994; accepted for publication 4 April 1994.

¹Forensic Chemist, Criminal Investigation Laboratory of Kyoto Prefectural Police H.Q., Kyoto, Japan.

Materials and Methods

Soil Samples

About 10 soil samples were collected from each of 110 different sampling sites (Fig. 1) in the Kyoto district, based on subsurface geological maps [8–10]. The soil samples were then dried at room temperature for three days and the grains larger than about 2 mm in diameter were removed. The unknown soil samples for a blind test were collected from 14 different sites by policemen.

X-ray Fluorescence Analysis (XRF)

About 2 g soil samples were ground to $-100 + 200$ mesh in a tungsten carbide mortar. Pellets were prepared at a pressure of about 10 ton/cm^2 using a vinyl chloride O-ring, 20 mm in diameter and 5 mm in depth, to contain the sample. A smaller size O-ring of 10 mm ϕ was used for 250 mg and 500 mg soil samples and an O-ring of 5 mm ϕ was used for 100 mg samples.

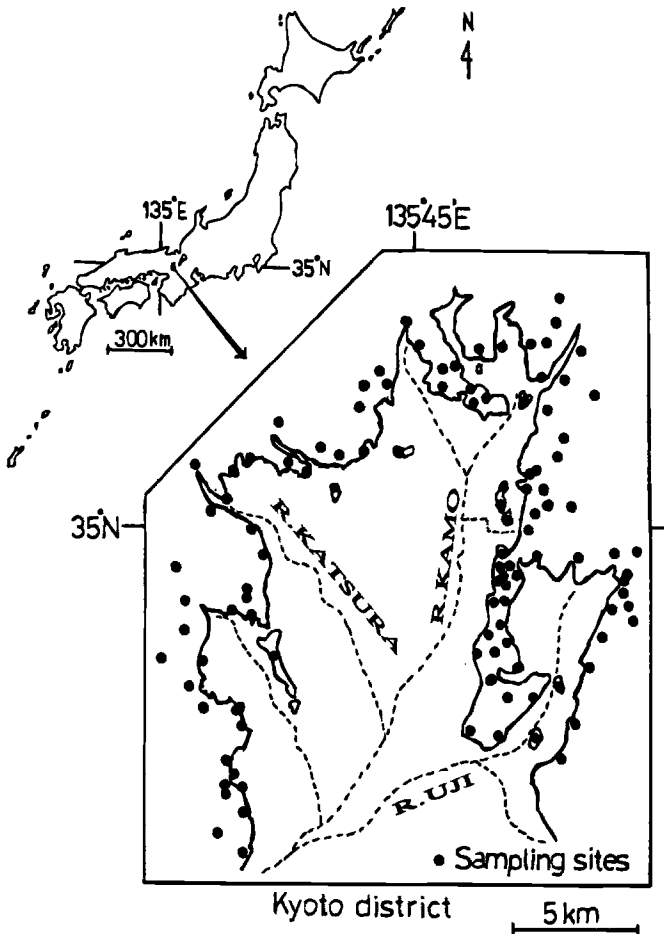


FIG. 1—Sampling sites for a geochemical survey map of soils.

Peak areas for seven elements—Si, K, Ca, Ti, Fe, Rb and Sr—were measured by the energy-dispersive X-ray fluorescence spectrometer RIGAKU-KeveX Subsystem 5000A and RIGAKU-KeveX ultra trace 0600 μ X system 7000. The standard rock sample, JG-1, was measured each time before 10 to 15 soil samples were measured. The analytical results of soils were normalized by JG-1 [11–14], in which the contents of Rb and Sr were equal to 181 ppm and 184 ppm, respectively [15]. Normalized values for each element are shown by barred element symbols such as \bar{K} .

Multivariate Analysis

Radar style charts using four elements (\bar{Rb} , \bar{Sr} , \bar{K} , and \bar{Fe}) were applied to characterize the chemical features of the soil samples. The radar chart was useful to exhibit the contents for four elements as a figure.

Furthermore, the principal component analysis using all seven elements and the discriminant analysis using four variations between two populations were applied to the analytical results. The former was useful to sum up and simplify analytical results on seven elements, and the latter was also useful to determine the soil type to which the unknown soil belongs.

Software for the multivariate analysis was developed using the PTOS-BASIC (NEC). A personal computer (NEC N5200-07 AD III) and an image reader (NEC N5266-02) were used.

Results and Discussion

Reproducibility of Soil Analysis by XRF

Nagatomo et al. [11] have obtained good calibration curves correlating peak areas and quantity for each element in silicate minerals measured by XRF. Table 1 shows the normalized results by JG-1 and coefficients of variation for 18 granitic soils collected from the same locality. They were analyzed using different types of X-ray fluorescence spectrometers. These analytical results showed good reproducibility for each element, and the coefficients of variation remained less than 20 percent, except for Ti. Thus, the method of normalization of XRF analytical results using JG-1 gave good analytical precision and a high degree of reproducibility.

The sensitivity limit of XRF was investigated using 100, 250, 500 and 2000 mg granitic soils. Figure 2 shows that samples larger than 250 mg gave a high degree of reproducibility, whereas 100 mg samples did not give reliable results for Si, K, Rb and Sr contents. This is probably because sufficient surface area and depth of a pellet for XRF analysis were not attained with 100 mg samples.

Soil Classification

The inorganic analytical results of soils were characterized by multivariate analysis in order to generate a geochemical survey map of soils. An accurate soil map was needed, using all available means, in order to predict the origins of unknown soils in practical forensic investigations.

Figure 3 shows the radar charts that indicate that soil samples in the Kyoto district can be classified into nine types. The trace elements, \bar{Rb} and \bar{Sr} , are most effective for all cases of soil characterization, \bar{Fe} is effective for the characterization of soils weathered from schalstein (clastic rocks of basaltic rock and/or lava), and \bar{K}/\bar{Rb} is effective for characterization of soils weathered from sedimentary rocks. Accordingly, the four elements—Rb, Sr, K and Fe—were found to be most effective for soil characterization, giving good agreement with geological rock types [16, 17].

The chemical and geological features of the soils, classified into nine types, are as follows:

TABLE 1—Results for reproducibility of granitic soils using different X-ray fluorescence spectrometers.

XRF SPL.	RIGAKU-KeveX System 5000A							RIGAKU-KeveX ultra trace 0600 μ X System 7000						
	Si	K	Ca	Ti	Fe	Rb	Sr	Si	K	Ca	Ti	Fe	Rb	Sr
No. 1	0.822	0.608	1.04	2.07	1.83	0.621	1.41	1.04	0.742	1.25	1.86	1.97	0.765	1.51
No. 2	0.970	0.775	0.850	1.23	1.24	0.730	1.20	0.850	0.829	0.865	1.15	1.30	0.693	1.09
No. 3	0.859	0.671	0.734	1.40	1.51	0.627	1.11	0.734	0.752	0.813	2.11	1.84	0.746	1.15
No. 4	0.945	0.878	0.991	1.47	1.27	0.689	1.16	0.991	0.948	1.07	2.06	1.36	0.827	1.52
No. 5	0.975	0.938	0.991	1.59	1.26	0.723	1.27	0.991	0.858	0.909	1.78	1.25	0.754	1.29
No. 6	0.948	0.877	1.06	1.26	1.09	0.666	1.24	1.06	0.821	0.929	1.61	1.14	0.724	1.22
No. 7	0.895	0.729	0.702	1.91	1.25	0.671	1.02	0.702	0.828	0.768	2.26	1.48	0.841	1.22
No. 8	0.937	0.705	0.794	1.90	1.43	0.718	1.14	0.794	0.828	0.859	2.56	1.67	0.819	1.23
No. 9	0.950	0.798	0.860	1.14	1.10	0.657	1.34	0.860	0.836	0.848	1.31	0.988	0.724	1.38
No. 10	1.02	0.730	0.976	1.65	1.13	0.624	1.43	0.976	0.761	1.03	1.51	1.31	0.659	1.52
No. 11	1.00	0.708	1.24	1.29	1.16	0.683	1.66	1.24	0.821	1.38	1.74	1.30	0.770	1.74
No. 12	0.971	0.786	1.04	1.46	1.20	0.684	1.26	1.04	0.978	1.24	1.89	1.55	0.900	1.51
No. 13	0.898	0.597	0.972	2.15	1.61	0.718	1.40	0.972	0.845	1.04	2.64	1.91	0.873	1.49
No. 14	0.813	0.597	0.900	2.11	1.64	0.647	1.37	0.900	0.772	1.06	1.71	1.26	0.711	1.51
No. 15	0.798	0.674	0.901	1.84	1.38	0.648	1.31	0.901	0.948	1.02	1.95	1.48	0.763	1.38
No. 16	1.01	0.780	0.999	1.48	1.10	0.648	1.44	0.999	0.848	1.03	1.58	1.19	0.707	1.45
No. 17	1.00	0.788	0.903	1.71	1.37	0.653	1.27	0.903	0.856	0.940	1.83	1.49	0.713	1.30
No. 18	0.967	0.758	1.30	2.36	1.60	0.676	1.38	1.30	0.827	1.30	2.52	1.74	0.741	1.40
A	0.932	0.753	0.959	1.67	1.34	0.671	1.30	0.959	0.828	1.02	1.89	1.46	0.763	1.38
σ	0.069	0.089	0.153	0.36	0.22	0.034	0.15	0.153	0.062	0.18	0.41	0.28	0.065	0.16
CV(%)	7.4	11.8	16.0	21.5	16.4	5.1	11.5	16.4	7.5	17.6	21.7	19.2	8.5	11.6
c	2nd. Target: Ti for Si, K and Ca in vacuum.													
o	(40kV-10mA)													
n	Mo for Ti, Fe, Rb and Sr in air.													
d	(40kV-20mA)													
i	Measuring time: 300 sec.													
t														
i														
o														
n														

NOTE: SPL, soil sample, A, average, σ, standard deviation; CV(%), coefficient of variation.

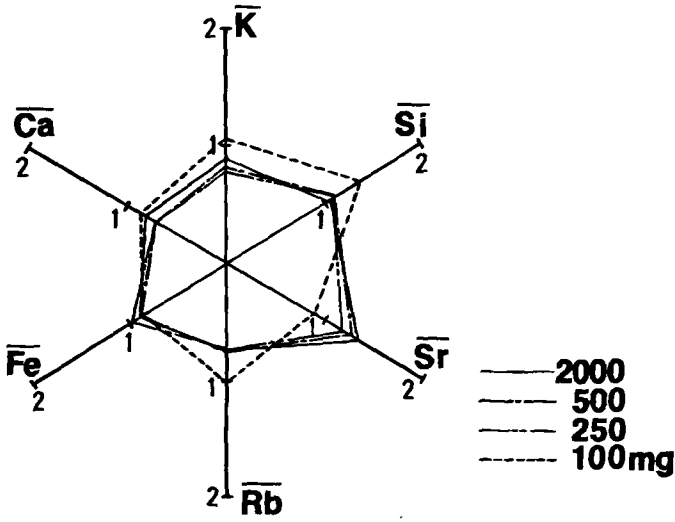


FIG. 2—Sensitivity limit of XRF analysis.

(a) **gr1**-type and **gr2**-type: granitic soils were classified into **gr1** and **gr2** types. Soils of **gr1**-type are rich in Sr and Ca, and those of **gr2**-type are rich in Rb and K.
 (b) **s1**-type and **s2**-type: soils of **s1**-type were weathered from sedimentary rocks (mainly chert) of the Paleozoic era, and **s2**-type from sedimentary rocks (mudstone, sandstone and/or chert) of the Mesozoic era. The Rb and K contents of **s1**-type soils are less than those of the **s2**-type. These two types are also characterized by the expression, $\bar{K} \cong \bar{Rb}$ (or $\bar{K}/\bar{Rb} = 1.1$).

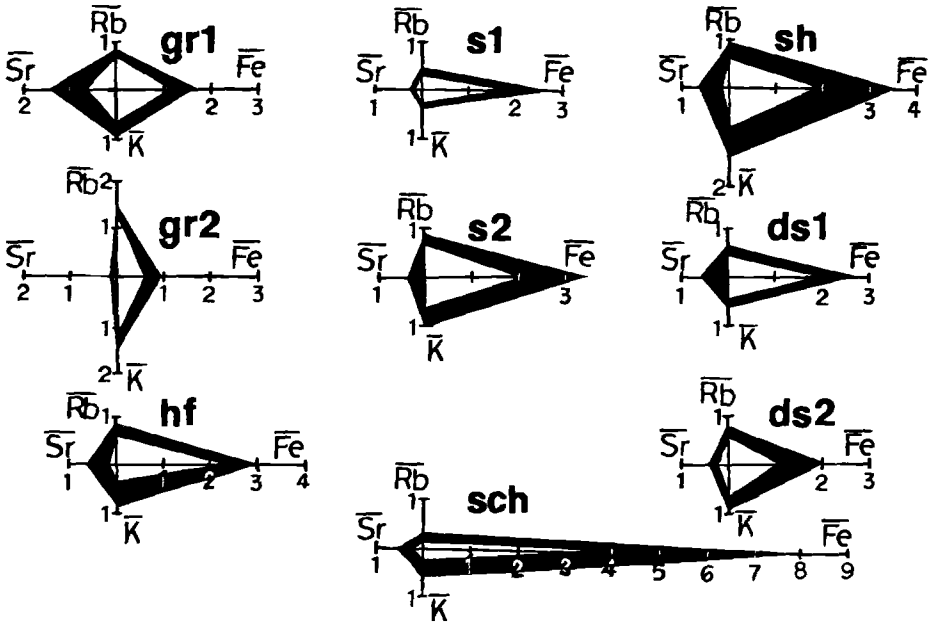


FIG. 3—Radar charts of nine soil types. Outer lines and inner lines indicate maximum and minimum of analytical results, respectively.

(c) **sch**-type and **sh**-type: soils of the **sch**-type were weathered from schalstein of the Mesozoic or Paleozoic era, and soils of the **sh**-type were weathered from argillaceous and/or siliceous rocks of the Paleozoic era. Soils of the **sch**-type are typically characterized by the largest values of $\overline{\text{Fe}}$. In addition, the **sch**-type and the **sh**-type are also characterized by the expression, $\overline{\text{K}} > \overline{\text{Rb}}$ (or $\overline{\text{K}}/\overline{\text{Rb}} = 1.5$).

(d) **hf**-type: soils of the **hf**-type were weathered from hornfels, and show intermediate chemical features between the **gr1**-type and the **s2**-type. That is, soils of the **hf**-type are similar to **s2**-type in $\overline{\text{Rb}}$, $\overline{\text{K}}$ and $\overline{\text{Fe}}$, but $\overline{\text{Sr}}$ values of the **hf**-type are larger than those of the **s2**-type.

(e) **ds1**-type and **ds2**-type: soils of **ds1** as well as the **ds2**-type are diluvial flood sediments of clay, sand and gravel. Chemical features of the **ds1**-type soil show an intermediate character between the **s1**-type and the **s2**-type, whereas those of the **ds2**-type are distinguished by smaller values of $\overline{\text{Fe}}$ than the **ds1**-type. Soils of the **ds1**-type were encountered in valleys, where **s1** and **s2**-type soils occur together; soils of the **ds2**-type were found in the lower parts of the Kyoto district, where fine sediments accumulate.

The chemical features of the nine soil types were confirmed by the principal component analysis. According to the calculations of eigenvectors and eigenvalues (Table 2), the high scores of the first principal component(I) represent higher contents of Rb and K, whereas the smaller I-component scores represent higher contents of Fe and Ti. In the second principal component(II), the larger II-component scores represent higher contents of Sr and Ca, whereas the smaller II-component scores represent higher content of Si (Fig. 4).

Population intervals of the nine soil types were investigated from the two groups-four variations ($\overline{\text{Rb}}$, $\overline{\text{Sr}}$, $\overline{\text{K}}$, $\overline{\text{Fe}}$)-discriminant analysis, calculating the Mahalanobis' generalized distance and the possibility of error [7,18]. The possibility of error (P_{A-B}), for example, the soil of A-group being mistaken for the B-group, was calculated according to the equation, $P_{A-B} = K_{A-B}/n_A$, where K_{A-B} is a number of samples mistaken to be B-group in n_A samples of A-group.

Results of the possibility of error were compiled in Table 3, and were shown to be less than 10% in most cases. Hence it is concluded that the discrimination among the nine soil types was worked out successfully. Successful discriminations were obtained when the Mahalanobis' generalized distances between two populations were above 10. Figure 5 shows these results and also the example of the most difficult discrimination among the **s2**-type, **ds2**-type and **hf**-type soils. In this case, the unknown soil turns out to be an **s2**-type because of its smallest Mahalanobis' generalized distance. Thus, the soil discrimination must be done allowing for the possibility of error when it is more than 10 percent. Nevertheless, soil types can generally be identified by their chemical features, as shown above.

TABLE 2—Eigenvectors and eigenvalues of principal component analysis applied to soil samples.

Principal component		I	II	III	IV
Eigenvector of correlation matrices	$\overline{\text{Si}}$	0.236	-0.488	-0.253	0.776
	$\overline{\text{K}}$	0.357	0.371	0.437	0.334
	$\overline{\text{Ca}}$	0.065	0.492	-0.488	0.110
	$\overline{\text{Ti}}$	-0.540	0.212	0.148	0.475
	$\overline{\text{Fe}}$	-0.555	0.205	0.207	0.183
	$\overline{\text{Rb}}$	0.440	0.253	0.452	0.083
	$\overline{\text{Sr}}$	0.141	0.479	-0.487	0.086
Eigenvalue		2.28	1.86	1.61	0.527
Proportion		0.362	0.296	0.257	0.084
Cumulative proportion		0.362	0.659	0.916	1.000

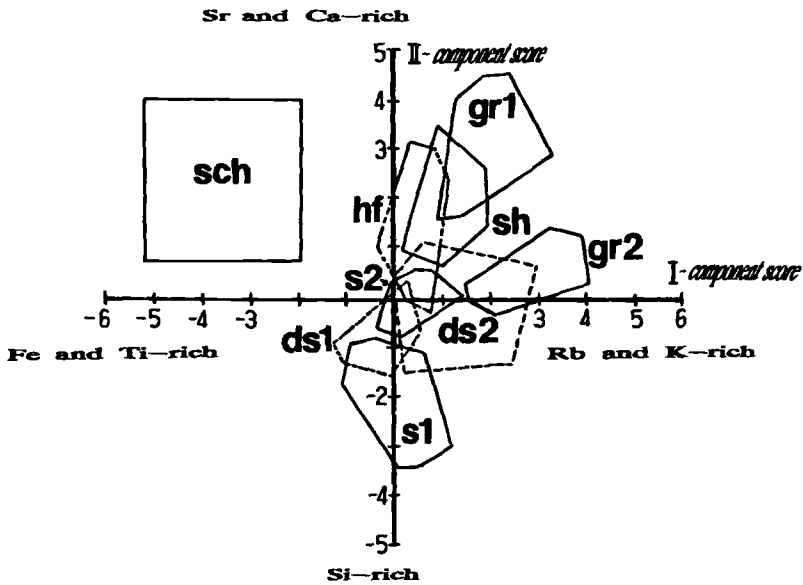


FIG. 4—Principal component score diagram of I-II.

Soil Discriminant System

The automated system to predict an unknown soil's origin was examined as a trial case. Figure 6 is the flow chart showing how the results can be achieved by multivariate analysis. The general procedure is as follows:

- (a) Users place the normalized XRF-analytical results of an unknown soil in the main memory area of computer.
- (b) The multivariate analysis, composed of radar chart, principal component analysis and discriminant analysis, are processed automatically, the results being displayed on a CRT graphics terminal.
- (c) Finally, users can obtain the information on the soil type and distributive localities of the unknown soil sample.

This system is supported by the control data sets and a geochemical survey map (Fig. 7) of nine soil types in the Kyoto district.

The soil discriminant system was subjected to the blind test on 14 additional soils which were collected in the Kyoto district. Using this system, correct predictions were made for 10 out of 14 blind soil samples, and the success rate was about 71%. Incorrect identification occurred in the discrimination of the *ds2*, *s2* and *hf*-types, where the a high possibility of errors had been observed.

This method suggests to be useful to compare known and questioned samples as well as to predict blind soil sample origins. Because four elements—Sr, Rb, K and Fe—are applicable to soil characterization and the radar chart using these elements is a useful technique to compare the chemical features of questioned soils with those of known soils.

However, the chemical feature described above is a profile of the soil. It is needless to say that the more useful soil discrimination is expected by combining information from the XRF analysis with that of other methods such as soil color matching, mineralogical analysis, X-ray diffraction and organic analysis.

TABLE 3—Possibility of error in discriminant analysis among nine soil types.

A/B	gr1	gr2	s1	s2	sch	sh	hf	ds1	ds2
gr1	(38)	0	0	0	0	2.6	0	0	0
gr2	(15)	...	0	0	0	0	0	0	0
s1	(78)	0	...	0	7.7	3.8	2.6	6.4	2.6
s2	(47)	0	0	...	0	17.0	6.4	6.4	3.6
sch	(43)	0	0	0	...	0	0	0	0
sh	(32)	0	0	0	0	...	4.0	0	0
hf	(25)	0	0	16.0	0	6.3	...	12.0	4.0
ds1	(57)	2.6	7.0	10.5	0	7.0	7.0	...	3.5
ds2	(38)	0	0	28.9	0	18.4	7.9	10.5	...

*1 Unit: %

*2 (value): Number of samples

*3 [Example]: The possibility of error that gr1(A group) may be mistaken for sh(B group) is 2.6 percent.

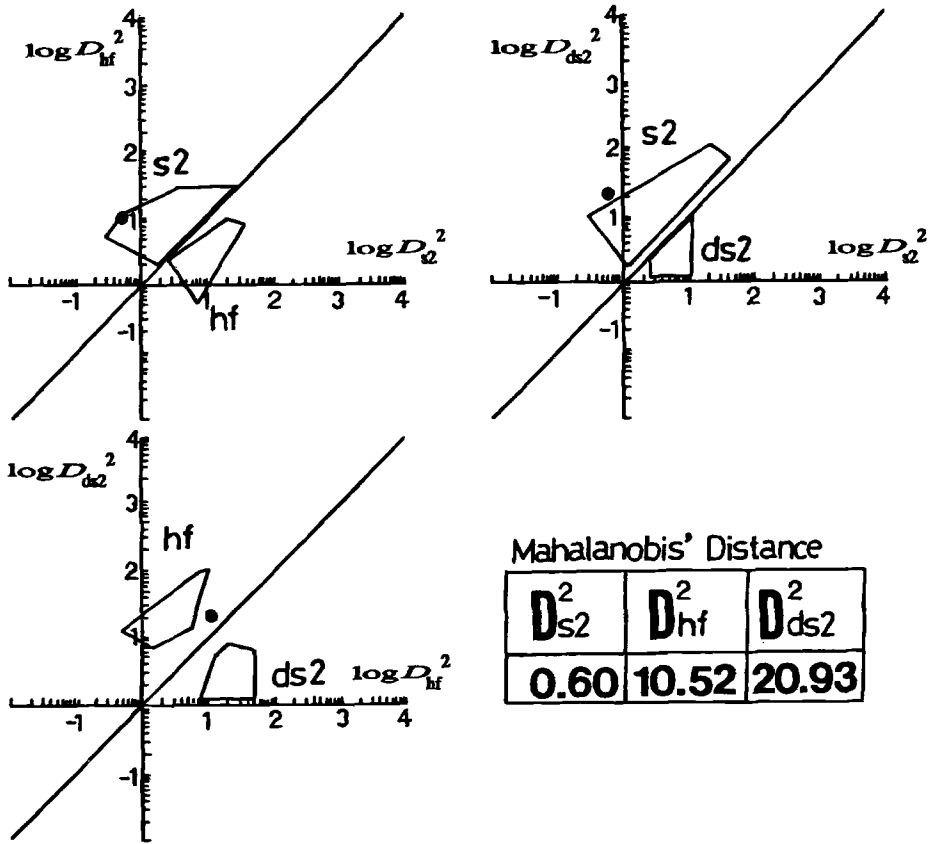


FIG. 5—Discrimination among s2-type, hf-type and ds2-type soils.

Conclusions

The results obtained suggest that inorganic analysis by XRF and multivariate analysis are useful to predict soil origins. This method offers the correct soil discrimination with a high probability and low personal error.

Besides the study area, it is necessary to apply this method to soil samples outside the Kyoto district. Nevertheless, geological and chemical features can be inferred for unknown soils even outside the study area by using the soil discriminant system and geological survey maps.

More accurate prediction and comparison of soil samples can be expected by combining information from XRF analysis with that given from other methods of soil characterization.

Acknowledgments

The author wishes to acknowledge the advice and help of Prof. T. Mitsuji of Nara University of Education and chief researcher T. Tsutsui of Kyoto Prefectural Institute of Hygienic and Environmental Science, who provided access to the X-ray fluorescence analysis. He also acknowledges the encouragement of Dr. S. Seta and Dr. Y. Marumo of National Research Institute of Police Science, Tokyo.

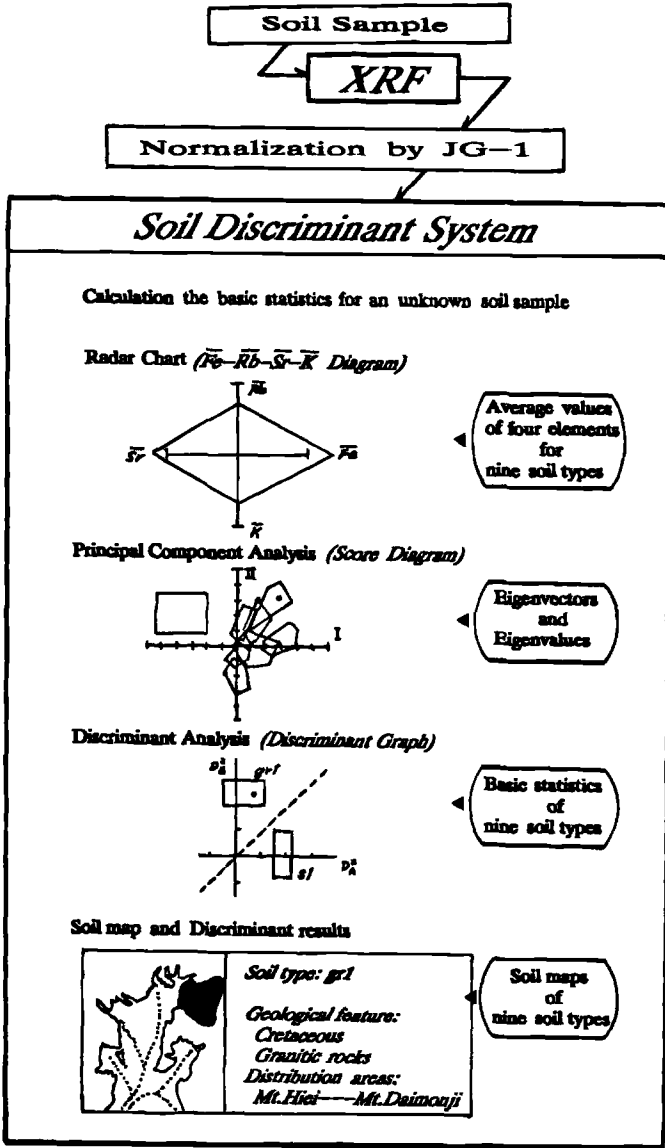


FIG. 6—Flow chart of the soil discriminant system.

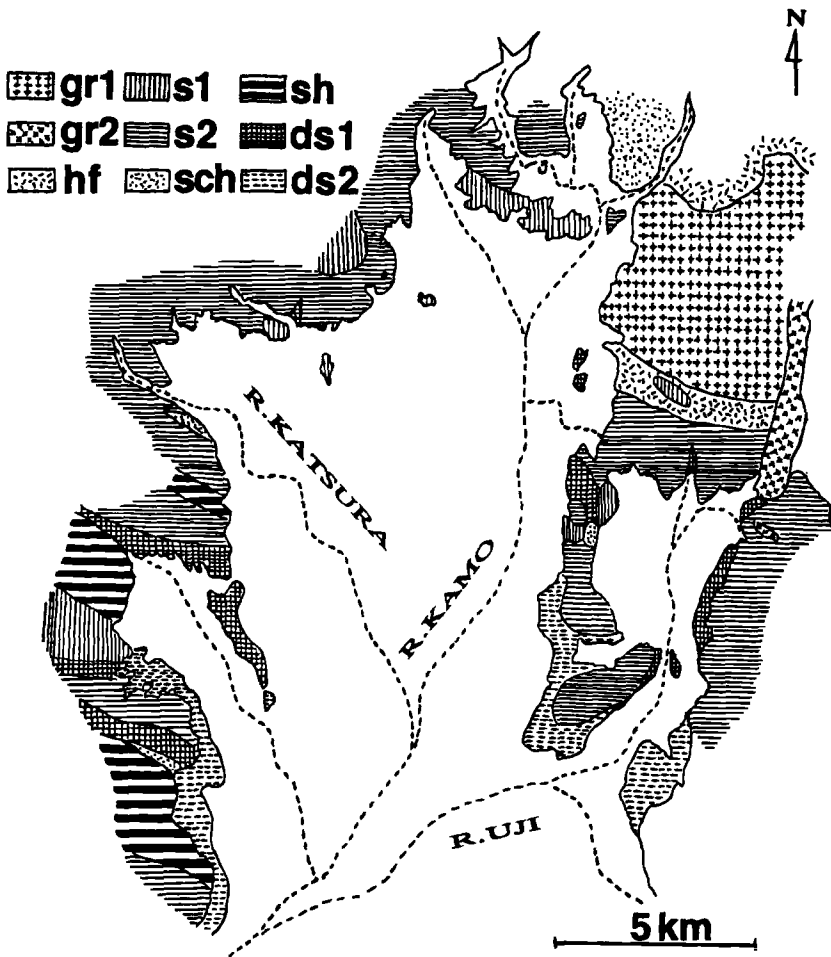


FIG. 7—Geochemical survey map of nine soil types in the Kyoto district.

References

- [1] Dudley, R. J., "The Use of Colour in the Discrimination Between Soils," *Journal of the Forensic Science Society*, Vol. 15, No. 3, July 1975, pp. 209–218.
- [2] Wanogho, S., Gettinby, G., and Caddy, B., "Particle Size Distribution Analysis of Soils Using Laser Diffraction," *Journal of the Forensic Science Society*, Vol. 33, 1987, pp. 117–128.
- [3] Nakayama, M., Fujita, Y., Kanbara, K., Nakayama, N., Mitsuo, N., Matsumoto, H., and Satoh, T., "Forensic Chemical Study on Soils. (I) - Discrimination of Area by Pyrolysis Products of Soil," *Japanese Journal of Toxicology and Environmental Health*, Vol. 38, No. 1, 1992, pp. 38–44.
- [4] Thornton, J. I. and McLaren, A. D., "Enzymatic Characterization of Soil Evidence," *Journal of Forensic Sciences*, Vol. 20, No. 4, Oct. 1975, pp. 674–692.
- [5] Marumo, Y., Nagatsuka, S., and Oba, Y., "Clay Mineralogical Analysis Using the <0.05 mm Fraction for Forensic Science Investigation—Its Application to Volcanic Ash Soils and Yellow-Brown Forest Soils," *Journal of Forensic Sciences*, Vol. 31, No. 1, Jan. 1986, pp. 92–105.
- [6] Marumo, Y. and Yanai, H., "Morphological Analysis of Opal Phytoliths for Soil Discrimination in Forensic Science Investigation," *Journal of Forensic Sciences*, Vol. 31, No. 3, July 1986, pp. 1039–1049.
- [7] Tanaka, Y. and Wakimoto, K., "Method of Multivariate Statistical Analysis," *Gendaisugaku-sha*, Kyoto, 1985, p. 296.
- [8] Miyamura, M., Komura, R., and Ishida, S., "Subsurface Geological Map, Kyoto-Seinanbu," The Economic Planning Agency, 1972.

- [9] Imoto, N., Musashino, M., and Ishida, S., "Subsurface Geological Map, Kyoto-Seihokubu," Kyoto Prefectural Government, 1981.
- [10] Tatekawa, M., Imoto, N., Musashino, M., and Ishida, S., "Subsurface Geological Map, Kyoto-Tohokubu-Kyoto-Tonanbu," Shiga Prefectural Government and Kyoto Prefectural Government, 1982.
- [11] Nagatomo, T., Miyake, Y., and Mitsuji, T., "Calibration Curves for Quantitative Analysis of Rock Samples Using an Energy Dispersive X-ray Analyser," *Bulletin of Nara University Education*, Vol. 35, No. 2, 1986, pp. 19-29.
- [12] Mitsuji, T. and Maruo, Y., "X-ray Fluorescence Analysis of Japanese Ancient Pottery 'Sueki'," *Advance in X-ray Chemical Analysis*, Vol. 10, 1978, pp. 61-66.
- [13] Mitsuji, T., Maruo, Y., and Nishioka, Y., "X-ray Fluorescence Analysis of the Sueware Sherds (Part 1). On the Chemical Features of the Sueware Sherds Produced in Western Japan," *Advance in X-ray Chemical Analysis*, Vol. 13, 1980, pp. 79-85.
- [14] Mitsuji, T. and Kojima, T., "X-ray Fluorescence Analysis of the Sueware Sherds (Part 2). On the Chemical Features of the Sueware Sherds Produced in the Chubu District," *Advance in X-ray Chemical Analysis*, Vol. 13, 1980, pp. 87-93.
- [15] Ando, A., "Standard Rock Samples," *Bunseki*, Vol. 8, 1978, pp. 526-535.
- [16] Hiraoka, Y., "X-ray Fluorescence Analysis for Soil Discrimination in Kyoto District," *Advance of X-ray Chemical Analysis*, Vol. 19, 1988, pp. 251-262.
- [17] Hiraoka, Y. and Mitsuji, T., "A Study on Local Characteristics of Soils (Part 1). Chemical Feature of Soils in Kyoto District," *Reports of National Research Institute of Police Science*, Vol. 42, No. 3, Aug. 1989, pp. 144-152.
- [18] Hiraoka, Y., "A Study on Local Characteristics of Soils (Part 2). The Discriminant Analysis of Soils," *Reports of National Research Institute of Police Science*, Vol. 42, No. 4, Nov. 1989, pp. 209-215.

Address requests for reprints or additional information to
 Y. Hiraoka
 Criminal Investigation Lab-Kyoto Prefectural Police H.Q.
 Kamanza-dori Shimotachiuri, Kamigyo-Ku, Kyoto 602
 Japan