Memoirs of the Faculty of Engineering, Okayama University, Vol.28, No. 1, pp.51-59, November 1993

# *Determination of Clay Minerals by the Ignition Loss Method Using a Muffle Furnace*

Iichiro KOHNO*, Kazuyasu TANABE** and Takemitsu TOMITA**

(Received Semtember 30 , 1993)

## SYNOPSIS

A technique for determining the layer structure and content of clay minerals was developed based on the relationship between temperature, and moisture characteristics of clay minerals. Moisture content in standard specimens, prepared by mixing montmorillonite, kaolinite and quartz in various proportions, was determined by measuring weight loss after heating. Based on the results from differential thermal analysis tests, the ignition loss method was found to be widely applicable to clays with montmorillonite and kaolinite as the main components. Dehydration of constituent water occurred at 530℃ and 800℃ in two- and three-layered clay minerals, respectively.

## 1. INTRODUCTION

Considerable research on engineering properties of soils has been reported in Soil Mechanics but studies on the relationships between clay minerals and their engineering properties are limited. This is probably because of the need to utilize complex analytical techniques such as X-ray diffraction, infrared absorption spectrum analysis and transmission electron microscopy. The development of simpler techniques for analyzing clay minerals, therefore, has become a focus of attention for various researchers.

Clay minerals were previously determined through measurements of cation exchange capacity, CEC (Alexaides and Jackson[1], Coffman and Fanning[2], Anzai and Yamamoto[3]). Differential thermal analysis (DTA) and thermogravimetry (TG), which were used to determine minerals such as kaolinite (Watanabe and Sugo[4], Karathanasis and Hajek[5]), indicated the existence of an association between the endothermic peak characteristics on the DTA curve and the reduction of weight on the TG curve. Kitagawa[6] reported that measuring weight loss after heating at 200℃ serves as a quick method for determining allophane non-crystalline inorganic components. Haruyama and Miyauchi[7] later showed that chemical properties and the degree of weathering were closely

* Department of Civil Engineering

** Department of Civil Engineering, Fukuyama University

related to each other in the ignition loss method. X-ray diffraction was used for determining montmorillonite content and was shown to be an effective method for providing clues to the stability of land and sliding surfaces (Tomita[8]). Thus all methods except DTA and TG require special skills as clay minerals are determined by their crystalline nature. In DTA, analysis is based on the peak temperature of endothermic or exothermic reaction that takes place upon heating. TG, which is used in combination with DTA, involves the measurement of changes in the weight of clay minerals following discharge of inter-layer water, adsorptive water and structural water at different temperatures. The objective of our investigation is to determine the optimum test conditions for the ignition loss method and to evaluate its applicability to a wide range of local samples.

## 2. MATERIALS AND METHODS

### 2.1 Sample Preparation

Samples included both terrestrial clays (from Nagano, Tottori and Onomichi) and marine clays (from Kasaoka, Fukuyama and Kure) collected from regions where landsliding is common. A two-layered clay mineral, kaolinite (Georgian kaolin, abbreviated as Kt) and a three-layered mineral, montmorillonite (Kunipia F, abbreviated as Mt) were used as standard samples while quartz (< 75 $\mu$m, abbreviated as Qt) served as a primary mineral. All samples were prepared as per Watanabe's method[9].

### 2.2 X-ray Diffraction

Following preparation of constant directional samples (Kitagawa et al.[10]), a Geiger Flex Model RAD-IIC with a monochromator (Rigaku Electric Co., Tokyo) was used under standard test conditions (Source: Cu-K ray (40 KV, 20 mA); Slit system DS; SS = 1, RS = 0.3 mm; Scanning speed 2mm/min).

### 2.3 Differential Thermal Analysis

DTA and TG were simultaneously conducted using Model TG/DTA 320 (Seiko Electronic Industries, Tokyo). A 15mg sample was filled in a platinum cell and the temperature was raised 10 ℃ / min. Alpha-alumina was used as reference material and measurements were taken in an azotic atmosphere (200 ml/ min). The peak surface area was calculated using Simpson's method (Nagashima[11]).

Prior to its application to test samples, DTA was applied to a specimen of Calcite ($CaCO_3$) of sufficiently advanced crystallization. The DTA-TG curve of calcite is shown in Fig. 1. A characteristic endothermic reaction occurred in the temperature range of 687-851℃ with a peak

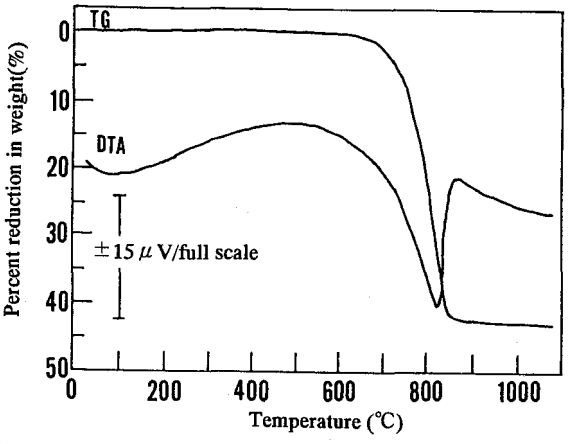



Fig.1. Differential thermal analysis (DTA) and thermogravimetry (TG) curves for calcite.

at 824℃. This was in contrast to data from Mackenzie[12], who reported the occurrence of endothermic reactions at a temperature range of 890–980℃. Such variation was probably related to differences in DTA procedures. Mackenzie used macro DTA with a minimum sample weight of 100 mg, while we used a micro DTA with a sample weight of 10–20mg. The endothermic peak and the reduction in weight occurred simultaneously. The reduction in weight caused by heating (42.2%) indicated in the TG curve was nearly equal to the theoretical value (44%) of reduction in weight following endothermic reaction of calcite ($CaCO_3 \rightarrow CaO + CO_2 \uparrow$).

### 2.4 Ignition Loss Method

A clay sample of approximately 1g (size < 2 $\mu$m) containing no organic matter was weighed in a 5ml magnetic crucible and placed in a desiccator at 55% relative humidity (RH adjusted with a saturated solution of magnesium nitrate) for 4 days (Sakamoto[13]). After measuring initial weight, the sample was dried in a muffle furnace (Koyo type I with temperature variation ± 2%) at 110℃ for 24 hours. The loss of weight was determined after cooling the contents to room temperature. This procedure was repeated after drying the sample at 530 and 800℃ for 24 hours. At least 3 samples were used in each measurement.

## 3. RESULTS AND DISCUSSION

### 3.1 Standard Samples

In a magnesium-saturated clay of the montmorillonite sample, diffraction peaked at 15.1 Å and moved to 18.2 Å following treatment with glycerol. In a potassium-saturated clay however, diffraction peaked at 12.0 Å and moved to 10.4 Å and 10.1 Å upon heating to 300℃ and 600℃, respectively. The main component was identified as pure montmorillonite.

In a magnesium-saturated clay of the kaolinite sample, a sharp diffraction peak appeared at 7.2 Å. In a potassium-saturated clay, the diffraction peak disappeared after heating to 600℃, indicating a structural breakdown. The main component here was determined to be kaolinite.

An endothermic peak occurred at 111℃ and again at around 615–800℃ in the montmorillonite sample. In the kaolinite sample, however, endothermic and exothermic peaks appeared at 546℃ and 997℃, respectively. The changes in weight in both samples occurred at the corresponding temperatures of endothermic peaks due to the loss of adsorptive water and desorption of structural OH (Fig. 2).

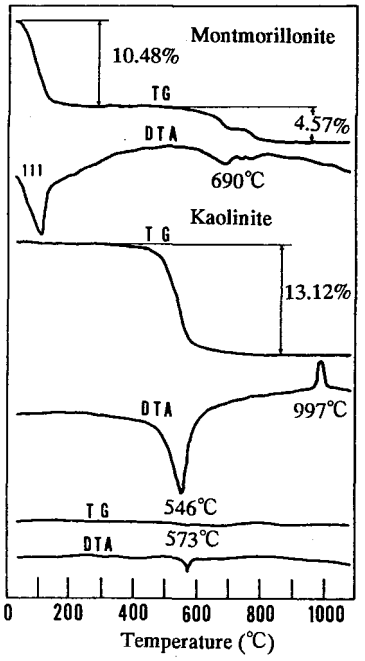



Fig.2. Differential thermal analysis(DTA) and thermogravimetry(TG) curves for standard samples

### 3.2 Artificially Mixed Samples

**(1) DTA Method:**

The amounts of structural water (4.57% and 13.12% in montmorillonite and kaolinite, respectively) estimated

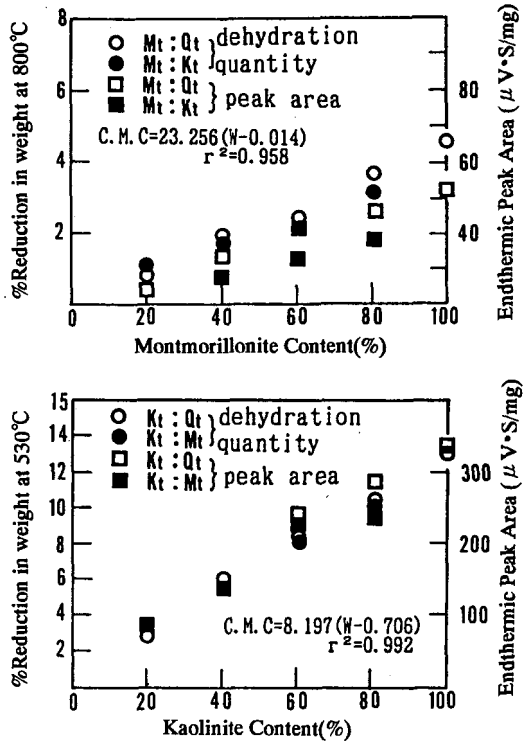



Fig.3. Relationships between reduction in weight upon heating and endothermic peak area vis-a-vis content of clay minerals

from DTA were largely similar to the theoretical values (5.01% and 13.94%, respectively) and were calculated using structural formulae of clay minerals. A strong positive correlation between the endothermic peak area and weight reduction was observed in both montmorillonite (r = 0.98**) and kaolinite (r = 0.99**) samples. A slight deviation in the strength of the correlation between clay minerals may have been caused by differences in shape of their respective endothermic peaks and/or minor errors in measurement. The reduction in weight upon heating increased with the proportions of clay mineral (Fig. 3).

**(2) Muffle Furnace Method:**

**Heating Temperature:** In montmorillonite, a considerable amount of inter-layer water was lost at 110℃ and 200℃. The loss of crystallization water occurred between 700 and 850℃ and a sufficient degree of dehydration occurred at 800℃. In kaolinite however, only 3 temperatures around 540℃ were selected for heating as peak endothermic temperature was about 546℃ (Fig. 2; Table 1). The reduction in weight of kaolinite was 12.06%, 12.09% and 12.42% following 6 hours of heating at 500, 530 and 550℃, respectively. If this rate of dehydration had continued, the reduction in weight following 24 hours of heating may have been between 13.4% and 13.7% rather than at the theoretical value of 13.9%.

Co-existence of minerals must also be taken into consideration in determining the heating temperature because dehydration of other minerals may overlap with that of kaolinite. For example, in illite, a three-layer clay mineral, there is a possibility of dehydration at 500-600℃ as part of the interlayer potassium is replaced by water. In view of this, we chose 530℃ to reduce the effect of such overlapping from other minerals. It may

Table 1. Heating assay of standard and artificially mixed samples

| Sample | Differential thermal analysis | | | Ignition loss test | | |
|---|---|---|---|---|---|---|
| | Reaction temperature (℃) | Weight change (%) | peak area ($\mu$v·s/mg) | % reduction in weight at 110℃ | % reduction in weight at 110℃ | % reduction in weight at 110℃ |
| Mt : Qt | | | | | | |
| 10 : 0 | 0–145 | 10.48 | 272 | 9.47 | | |
| | 615–805 | 4.57 | 64 | | 1.74 | 5.22 |
| 8 : 2 | 0–145 | 7.97 | 210 | 7.68 | | |
| | 601–822 | 3.68 | 54 | | 1.73 | 4.08 |
| 6 : 4 | 0–130 | 5.77 | 149 | 5.72 | | |
| | 601–802 | 2.42 | 42 | | 1.22 | 3.06 |
| 4 : 6 | 0–123 | 4.33 | 104 | 3.80 | | |
| | 613–797 | 1.84 | 28 | | 0.96 | 1.95 |
| 2 : 8 | 0–106 | 2.00 | 42 | 2.08 | | |
| | 655–792 | 0.82 | 8 | | 0.48 | 1.03 |
| 0 : 10 | - | - | - | 0.07 | 0.06 | 0.02 |
| Kt : Qt | | | | | | |
| 10 : 0 | 470–593 | 13.12 | 331 | 0.53 | 14.33 | 0.87 |
| 8 : 2 | 458–588 | 10.41 | 282 | 0.35 | 11.27 | 0.81 |
| 6 : 4 | 453–581 | 8.32 | 237 | 0.29 | 9.25 | 0.68 |
| 4 : 6 | 475–591 | 5.89 | 144 | 0.12 | 5.37 | 0.47 |
| 2 : 8 | 448–573 | 2.79 | 77 | 0.10 | 2.61 | 0.22 |
| Mt : Kt | | | | | | |
| 8 : 2 | 0–145 | 7.46 | 195 | 7.92 | | |
| | 460–573 | 3.32 | 81 | | 3.83 | |
| | 657–812 | 3.12 | 36 | | | 4.36 |
| 6 : 4 | 0–138 | 6.03 | 153 | 5.97 | | |
| | 458–593 | 5.48 | 137 | | 6.42 | |
| | 657–805 | 2.19 | 26 | | | 3.58 |
| 4 : 6 | 0–135 | 4.50 | 109 | 4.26 | | |
| | 458–596 | 7.98 | 217 | | 8.76 | |
| | 637–797 | 1.71 | 14 | | | 2.89 |
| 2 : 8 | 0–126 | 2.82 | 59 | 2.44 | | |
| | 473–586 | 9.85 | 238 | | 11.52 | |
| | 652–808 | 1.12 | 8 | | | 1.82 |
| Calcite | 687–851 | 42.20 | 638 | | 0.07 | 45.03 |

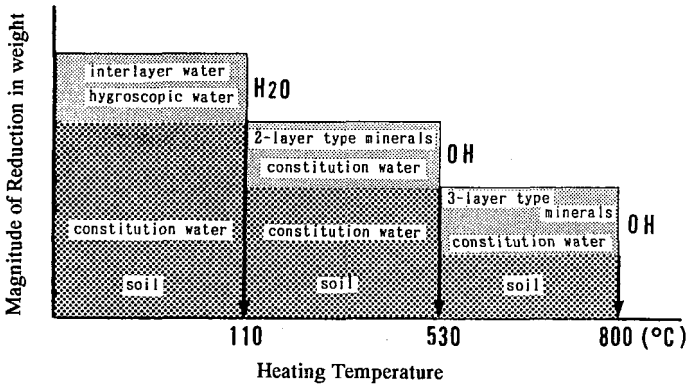



Fig.4. Diagram illustrating difference in loss of moisture in various clay minerals at different temperatures

therefore be concluded that dehydration of inter-layer water occurs at 110℃ and dehydration of constituent water occurs at 530℃ and 800℃ in two- and three-layered clay minerals, respectively. These results may be diagrammatically illustrated as in Fig. 4.

**Sample Weight:** The loss of interlayer water at 110℃ increased as sample weight increased, but the loss of structural OH at 530 and 800℃ tended to decrease (Fig. 5). A comparison of values for moisture loss in DTA

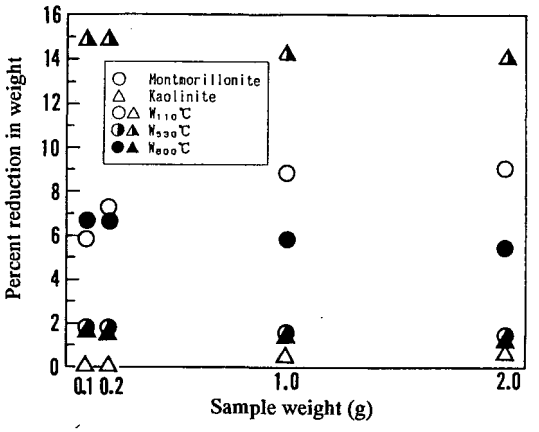



Fig.5. Relationships between the reduction in weight(%) and sample weight

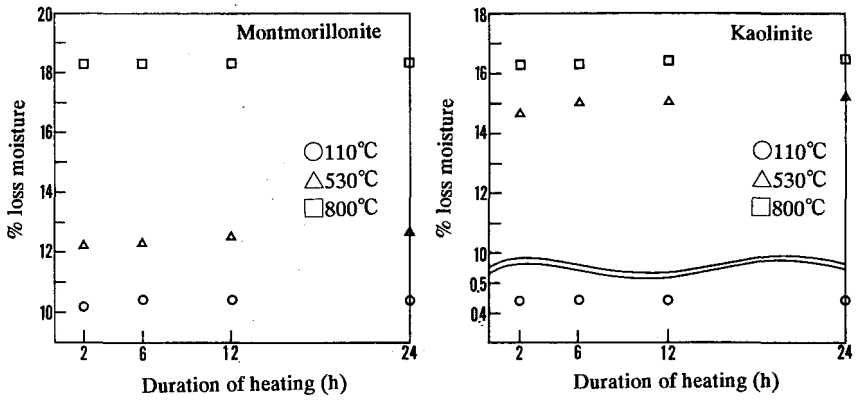



Fig.6. Relationships between amount of moisture loss and heating time

and TG (Fig. 2) indicated that the loss of moisture was consistent when weight of the sample was around 1g. Since the error is likely to become large if the weight of the sample is too small, the optimum weight for analysis was set at 1g.

**Heating duration:** The rate of dehydration increased within a short period and reached a plateau within 6–12 hours (Fig. 6 a,b). In light of this, a heating period of 24 hours was considered appropriate.

**Applicability of Ignition Loss Method:** A positive relationship between the amount of water lost upon heating and the amount of clay mineral in the mixture was found (Fig. 7). The estimated values of clay mineral content in different mixtures (Table 2) closely corresponded with actual values, thereby indicating the applicability of the muffle furnace method.

### 3.3 Local Samples

**Identification of Clay Minerals:** Prior to using the ignition loss method, clay minerals in local samples were

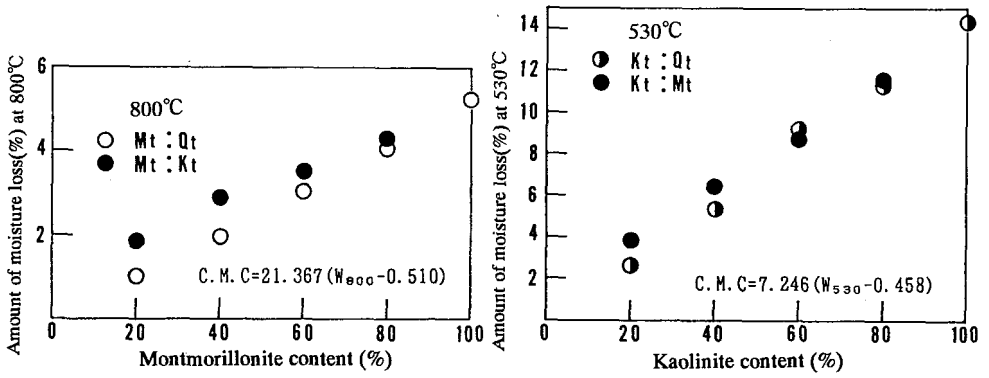
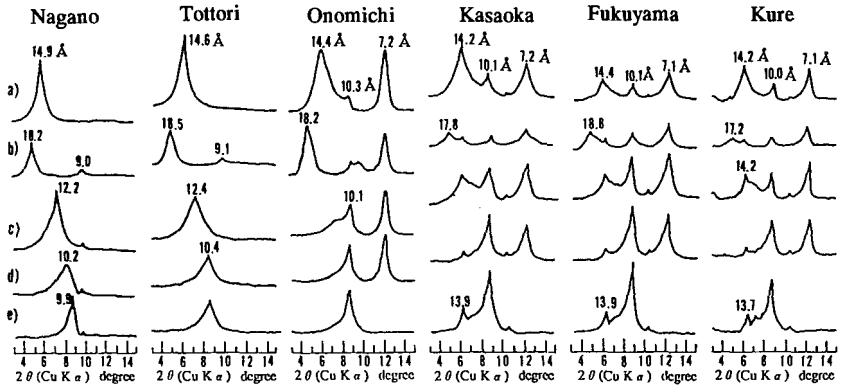



Fig.7. Relationships between moisture content and content of clay minerals

Table 2. Estimated values of clay mineral content for standard samples

| Mt:Qt | Content of 3 -layer mineral(%) | Kt:Qt | Content of 2 -layer mineral(%) | Mt:Kt | Content of 3 -layer mineral(%) | Content of 2 -layer mineral(%) |
|---|---|---|---|---|---|---|
| 10:0 | 100.6 | 10:0 | 100.5 | 10:0 | 100.6 | 9.3 |
| 8:2 | 76.3 | 8:2 | 78.3 | 8:2 | 82.3 | 24.4 |
| 6:4 | 54.5 | 6:4 | 63.7 | 6:4 | 65.6 | 43.2 |
| 4:6 | 30.8 | 4:6 | 35.6 | 4:6 | 50.9 | 60.2 |
| 2:8 | 11.1 | 2:8 | 15.6 | 2:8 | 28.0 | 80.2 |
| 0:10 | - | 0:10 | - | 0:10 | 6.7 | 100.5 |




a )$Mg^{2+}$ saturated,normal temperature b )$Mg^{2+}$ saturated,glycerol treatment
C)$K^{+}$ saturated,normal temperature d )$K^{+}$ saturated,300℃ e )$K^{+}$ saturated,600℃

Fig.8. X-ray diffraction patterns for local samples

examined by X-ray diffraction, DTA and TG (Figs. 8 and 9) . Of the terrestrial clays, the samples from Nagano and Tottori contained montmorillonite, while those from Onomichi had montmorillonite and kaolinite. Marine clays from Kasaoka, Fukuyama and Kure contained montmorillonite, kaolinite, nontronite and mica minerals.

**Application of Ignition Loss Method:** In general, the results from the ignition loss method were largely similar to those obtained by X-ray diffraction, DTA and TG (Table 3). A few differences between the results from DTA

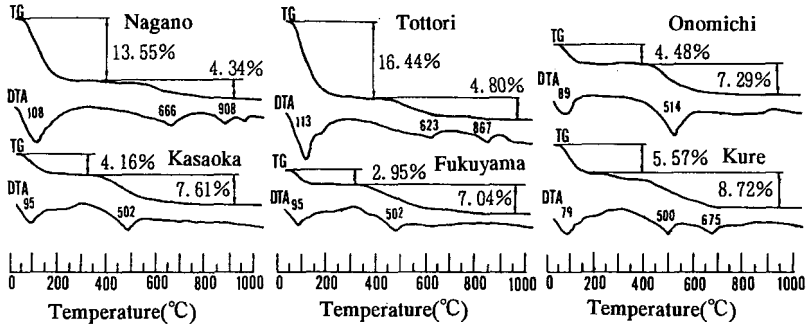



Fig.9. Differential thermal analysis(DTA) and thermogravimetry(TG) curves for local samples

Table 3. Heating assay of local samples

| Sample | Differential thermal analysis: Reaction temperature (℃) | Weight change (%) | peak area (μv·s/mg) | Ignition loss method: % reduction in weight at 110℃ | % reduction in weight at 110℃ | % reduction in weight at 110℃ |
|---|---|---|---|---|---|---|
| Nagano | 0–232 | 13.55 | 415 | 13.44 | | |
| | 232–571 | 1.62 | – | | 1.14 | |
| | 571–999 | 2.72 | 79 | | | 3.86 |
| Tottori | 0–229 | 16.44 | 310 | 16.56 | | |
| | 229–491 | 1.65 | – | | 2.09 | |
| | 491–980 | 3.15 | 45 | | | 3.72 |
| Onomichi | 0–158 | 4.48 | 108 | 3.08 | | |
| | 158–578 | 6.12 | 167 | | 6.48 | |
| | 578–980 | 1.17 | – | | | 1.56 |
| Kasaoka | 0–167 | 4.16 | 95 | 4.21 | | |
| | 167–548 | 5.77 | 66 | | 7.35 | |
| | 548–999 | 1.84 | – | | | 2.17 |
| Fukuyama | 0–144 | 2.95 | 68 | 3.56 | | |
| | 144–543 | 5.22 | 44 | | 6.66 | |
| | 548–999 | 1.82 | – | | | 2.07 |
| Kure | 0–153 | 5.57 | 107 | 3.38 | | |
| | 153–559 | 6.08 | 54 | | 7.91 | |
| | 559–999 | 2.64 | – | | | 2.26 |

Table 4. Estimated values for clay mineral content of local samples

| Sample name | Differential thermal analysis: Content of 2-layer mineral(%) | Content of 3-layer mineral(%) | Ignition loss test: Content of 2-layer mineral(%) | Content of 3-layer mineral(%) |
|---|---|---|---|---|
| Nagano | 7.5 | 62.9 | 4.9 | 71.6 |
| Tottori | 7.7 | 72.9 | 11.8 | 68.6 |
| Onomichi | 44.4 | 26.9 | 43.6 | 22.4 |
| Kasaoka | 41.5 | 42.5 | 49.9 | 35.5 |
| Fukuyama | 37.0 | 42.0 | 44.9 | 33.3 |
| Kure | 44.1 | 61.0 | 54.0 | 37.4 |

(Table 4) and estimated values were observed, however, probably due to differences in conditions of measurement and the range of temperatures used for analysis.

Our results suggest that the ignition loss method using a muffle furnace may be used effectively for different samples containing montmorillonite and/or kaolinite as the main components. Further studies are required, however, to apply this method to soils of a more general nature. For example, this method cannot be used for serpentine materials derived from basic rocks as endothermic peaks caused by the dehydration of structural water

occur at 600–700℃. Studies are also necessary to examine the influence of mixing hydrated oxides (gibsite, gatite, illite, vermiculite, chlorite, etc.), and to determine the broad applicability of the method in soils having montmorillonite and kaolinite as mixed layer minerals.

## 4. CONCLUSIONS

Our studies clearly demonstrated that (a) the ignition loss method was simple and applicable to soils containing montmorillonite and/or kaolinite, (b) determination of clay minerals was possible at 530℃ and 800℃ in two–and three–layered clay minerals respectively, (c) there was a good correlation between the content of clay minerals and dehydration of structural OH (based on comparative evaluation of results from DTA, TG and ignition loss method), and (d) a good correspondence among results from local samples, with respect to layer structure, was found using X–ray diffraction and ignition loss method.

## REFERENCES

(1) C.A. Alexaides and M.L. Jackson, "Quantitative determination of vermiculite in soils," Soil Sci. Soc. Am. Proc., 29, pp. 522–527, (1965).

(2) C.B. Coffman and D.S. Fanning, "Vermiculite determination in whole soils by cation exchange capacity methods," Clays Clay miner., 22, pp. 271–283, (1974).

(3) T. Anzai, and K. Yamamoto, "Characteristics of soil clays in Chiba Prefecture and their contribution to soil productivity –1:2:1 and 2:1:1 layer silicate intergrades in soil from the tertiary in Chiba Prefecture," Japan J. Soil Sci. Pl. Nutr., 56 (2), pp. 85–91, (1985), in Japanese.

(4) Y. Watanabe and S. Sogo, "An application of simultaneous differential thermal analysis and thermogravimetry to quantitative estimation of Kaolin materials and Gibsite in soils," Treatise on clay minerals, pp. 210–214, (1975).

(5) A.D. Karathanasis and B.F. Hajek, "Revised methods for rapid quantitative determination of minerals in soil clays," Soil Sci. Soc. Am. J., 46, pp. 419–425, (1982).

(6) Y. Kitagawa, "Rapid methods for determination of Allophane and amorphous inorganic materials," J. Sci. Soil Manure, Japan, 48(4), pp. 124–129, (1977), in Japanese.

(7) M. Haruyama and N. Miyauchi, "The physico–chemical properties of ground having Pumice flow deposit and volcanic ash," J. Japan Soc. Soil Mech. Found. Eng., 20(1), pp. 103–111, (1980), in Japanese.

(8) T. Tomita, "A study on physico–chemical techniques of landslide and its countermeasure," Doctorate thesis at Kyoto University, pp. 23–39, (1981), in Japanese.

(9) Y. Watanabe, "Sampling of soil–forming," Kodansha, pp. 34–56, (1976), in Japanese.

(10) Y. Kitagawa, K. Yamamoto and Y. Watanabe, "The properties of inter–stratified minerals occurring in two soils," J. Sci. Soil Manure, Japan, 46(12), pp. 521–528, (1975), in Japanese.

(11) H. Nagashima, "Numerical calculation," Maki Pub. Co., pp. 73–114, (1979), in Japanese.

(12) R.C. Mackenzie, "Differential thermal analysis," Academic Press, London, pp. 497–537, (1970).

(13) T. Sakamoto, "Differential thermal analysis of smectite with special reference to endothermic peaks around 100℃, " J. Mineral. 17, pp. 147–153, (1986), in Japanese.