Rapid Determination of Allophane and Amorphous Inorganic Materials in Soils

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Allophane, a dominant clay mineral in andosols (volcanic ash soils), has large surface area, high water-holding capacity, high phosphorus absorption and fixation capacity, strong affinity with humic substances, and feeble bonding forces between particles. These properties of allophane are also the characteristics of andosols, and the clarification of its content is necessary to manage and estimate the fertility of these soils. Kitagawa[1,2] examined five methods for the determination of allophane and amorphous inorganic materials (AIM) in soil clay fractions, i.e., an alternate dissolution with HCl and NaOH solution by Segalen[3], a dissolution with 0.5 N NaOH by Hashimoto and Jackson[4], a dissolution with acid ammonium oxalate solution by Tamm[5], the cation-exchange capacity delta value of allophane by Aomine and Jackson[6], and a new method based on the difference of weight by heating between 105 and 200°C. It was concluded that the alternate dissolution with HCl and NaOH solution is suited for the purpose, and the new method based on the weight loss by heating at 200°C is sufficiently applicable to routine analysis which is required to treat a great deal of sample as a rapid one although the values are approximate, while, the other three are not so good as the formers.

Definition of allophane and amorphous inorganic materials

Allophane has not clearly defined yet. In this paper, allophane and AIM are regarded as follows: Allophane is a naturally occurring mineral which is amorphous or poorly crystallized[7], is composed of silica, alumina, water, a little of iron and bases varied in relatively wide range under a certain rule[8], contains large amounts of specific water as mentioned later, consists of a microaggregate of "unit particle" about 50 Å in diameter, and has large specific surface area of several hundreds m^2/g regarded as external surface[9]. X-ray diffraction pattern of allophane frequently shows weak hallos near 3.5 and 2.3 Å, and no sharp peak[10], differential thermal analysis curve displays a large endotherm below 200°C and a sharp exotherm above 800°C with no intermediate peak[11], and infrared absorption bands associated with O-H and Si-O stretching vibration are broad with maximum near 3500 and 1000 cm^{-1}, respectively[12]. The previous studies on the water in allophane[12,13,14,15] characterized that; the OH groups are on the surface and unstable, very long time is required for the dehydration to be finished by heating at constant temperature, and the adsorbed water also has the histeresis between dehydration and rehydration.

AIM was termed allophane analogues of silicates and weathered inorganic gels of silica, alumina and iron oxides occurring in soils, which are amorphous to X-rays.

Procedures of quantitative determination

The flow sheet for the quantitative determination of allophane and AIM by means of the alternate dissolution with HCl and NaOH

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About 2 g of air-dried soil
- —Decompose organic materials with 10% H_2O_2
- —Wash with distilled water
- —Centrifugalize

1 g of soil dried at 105°C for 24 hr in weight-known glass centrifuge-tube
- —50ml of 8N HCl
- —Shake for 30 min
- —Centrifugalize

Precipitation
- —Wash with distilled water
- —50ml of 0.5N NaOH
- —Warm in boiled water-bath for 5 min
- —Centrifugalize

Precipitation (Repeat)
- —Wash with distilled water
- —Dry at 105°C for 24 hr

Determine weight loss

Fig. 1. Flow sheet for quantitative determination of allophane and AIM by means of the alternate dissolution with 8 N HCl and 0.5 N NaOH.

About 3 g of air-dried soil
- —Wash with 1N KCl
- —Centrifugalize

Precipitation
- —Decompose organic materials with 10% H_2O_2 in alkaline solution
- —Wash with alkaline 1N KCl
- —Wash with neutral 1N KCl
- —Wash with distilled water 2 times
- —Centrifugalize

Precipitation
- —Air dry

About 2 g of precipitation
- —Dry at 105°C for 24 hr, (A)
- —Dry at 200°C for 24 hr, (B)

Weight loss, (A—B)

Fig. 2. Flow sheet for the determination of weight loss by heating at 200°C.

solution, which is a method for obtaining the exact values is shown in Fig. 1: First, 1 g of soil sample dried at 105°C for 24 hr after decomposed organic materials with 10% H_2O_2 is weighed into glass centrifuge-tube of which weight is known, add 100 ml of 8 N HCl, stopper and shake for 30 min. After centrifugation at 2000 rpm for 5 min, the precipitation is washed once with distilled water, then suspended in 100 ml of 0.5 N NaOH, warmed for 5 min in boiled-water bath, and centrifugalized. This procedure is repeated for required rounds. The precipitation is washed with distilled water after the final treatment with 0.5 N NaOH, centrifugalized, and dried at 105°C for 24 hr. The weight loss with this procedure is determined by weighing. The contents of allophane and AIM are obtained from the weight loss with the procedure based on the following principle suggested by Segalen[3]: In HCl and NaOH solutions, AIM is dissolved far more rapidly than crystalline minerals. When a soil containing allophane and AIM is treated alternately with HCl and NaOH solution, the sum of the dissolved components increases rapidly at the initial stage, but it soon does gradually and linearly. The contents of allophane and AIM are obtained from the value at the intersection of ordinate and the extention of the linear part of the dissolution curve, when the number of rounds and weight loss in the alternate dissolution with HCl and NaOH solution are represented in abscissa and ordinate, respectively.

The flow sheet of the new method proposed in this study for the quantitative determination of allophane and AIM in soils based on the weight loss by heating at 200°C is shown in Fig. 2. First, organic materials which coexist in soil samples are decomposed with H_2O_2 solution. About 3 g of soil sample is put into a tall-beaker after washed with 50 ml of 10% H_2O_2 warming on a hot-plate. To the suspension, 10 ml of 30% H_2O_2 is added anew after vigorous bubbles disappeared, if the soil color is still dark. When the dark color has been lightened, the pH value of suspension is adjusted to 8–9 with KOH solution, and further treated with the H_2O_2 solution. After this step is repeated several times, the suspension is centrifugalized. The precipitation is washed with alkaline 1 N KCl, neutral 1 N KCl and two times distilled water, successively, then air-dried. About 2 g of this sample is exactly weighed after drying at 105°C for 24 hr in a weighing-tube, then also dried at 200°C for 24 hr. The percentage of this loss is calculated from a formula, 100(A-B)/A, where A and B is the weight dried at 105 and 200°C, respectively. The practical method for the determination of allophane and AIM will be discussed in the end of this paper.

Soil samples

The soil samples are listed in Table 1. Nine and three andosols were collected from Japan and Indonesia, respectively. Other three soils were also used for the reference. The dominant minerals are allophane and AIM in all the clay fractions of these andosols. On the other hand, kaolin minerals or dioctahedral vermiculite are dominant in the clay fraction of 31–2, unvolcanogenous red-yellow deluvial soil; 32–1, unvolcanogenous humic deluvial

Table 1. Soil samples

No. Hor. (cm) Color	Texture	pH (1 : 1H_2O)	Total-C (%)	Location and land use
ANDOSOLS				
1-2(0-5) 10 YR 2/1	SL	5.9	7.60	Bekkai, Nemuro, Hokkaido, Unused
-5(19-28) 10 YR 2/1	L	6.2	4.59	
6-1(0-44) 5 YR 2/2	L	5.8	10.04	Akahira, Shimokuriyagawa, Morioka, Iwate ; Pine forest
-5(114-) 7.5 YR 5.5/8	SiCL	6.4	1.46	
9-1(0-18) 7.5 YR 4/4	SL	5.3	2.12	Egi, Maebashi, Gunma ; Upland field
-5(88-109) 7.5 YR 6/8	L	6.0	0.52	
12-2(18-25) 7.5 YR 2/2	CL	5.9	4.56	Miyagasaki, Ibaraki, Ibaraki ; Upland field
-5(90-135) 10 YR 4/6	SL	6.5	1.19	
14-2(18-30) 7.5 YR 2/2	C	6.0	5.74	Mito, Hatsuse, Miura, Kanagawa ; Upland field
-6(100-) 7.5 YR 4/6	SL	6.6	1.52	
21-1(0-9) 10 YR 2/1	SiCL	5.8	7.59	Minamikumai, Shiojiri, Nagano ; Mulberry field
-5(75-100) 10 YR 4.5/6	L	6.0	2.00	
23-1(0-13) 5 YR 1/1	CL	5.3	19.10	Tomiyamane, Yatsuka, Okayama ; Grass land
-5(90-) 10 YR 5/4	LS	5.5	0.87	
25-2(20-38) N1	CL	5.5	19.49	Sawamizu, Kuju, Oita ; Grass land
-6(109-) 10 YR 3/3	SL	5.8	1.81	
29-1(0-12) 7.5 YR 2/3	SL	6.3	4.20	Okubo, Ei, Kagoshima ; Upland field
-4(25-55) 10 YR 3/3	LS	6.8	0.31	
IN4-1(0-16) 10 YR 2/2	CL	6.2	6.25	Block Kramat, Afd, Sukamantri, Kotabatu, Bogor, West Java ; Low-land rice field
IN15-1(0-20) 7.5 YR 2/1.5	L	6.0	8.57	Batureok, Tjikahuripan, Lembang, Bandung, West Java ; Upland field
IN30-1(0-50) 10 YR 2.5/2	L	6.0	7.15	Karangduren, Salatiga, Semarang, Central Java ; Upland field
OTHER SOILS				
31-2(12-) 5 YR 5/8	C	4.8	0.41	Mikatabara, Hamamatsu, Shizuoka ; Upland field
32-1(0-35) 7.5 YR 2/1	C	4.0	12.08	Kanaya, Shizuoka ; Unused
IN1-1(0-15) 10 YR 4/4	C	5.4	1.83	Kedung Halang, Bogor, West Java ; Low-land rice field

soil; and IN1-1, latosol.

The weathered pumice from Kanumatsuchi bed was used for a standard sample. The air-dried one smaller than 100 mesh was employed in the measurement.

Result and discussion

In the soil samples from which organic materials were removed with H_2O_2 solution, the correlation between the allophane and AIM contents obtained from the alternate dissolution with 8 N HCl and 0.5 N NaOH, and the weight loss by heating at 200°C is shown in Fig. 3, where the former is expressed in the ordinate, and the latter in the abscissa. The regression equation was $y=12.0x-1.3$, and the correlation coefficient was 0.97. The linear correlation was established with the 99.9% confidence limit. This suggests the certainty of application of the weight loss by heating at 200°C to rapid determination of allophane and AIM in soils. The above equation is approximate to $y=12x$. This equation was applicable when the weight loss of the Kanumatsuchi allophane was estimated at 8.53%. The allophane content in Kanumatsuchi sample used here as the standard was 69%, and the weight loss of the sample at 200°C was 5.89%.

To prevent the error, the standard sample of which allophane and AIM contents are already known must be heated in parallel with test samples, because it is very difficult to make the constant condition in every measurement of the weight loss at 105 and 200°C. A large problem in the measurement of weight loss should be the temperature distribution inside the oven. This problem, however, should be dissolved by using an air-circulated oven.

The determination method of allophane and AIM in soils based on the weight loss by

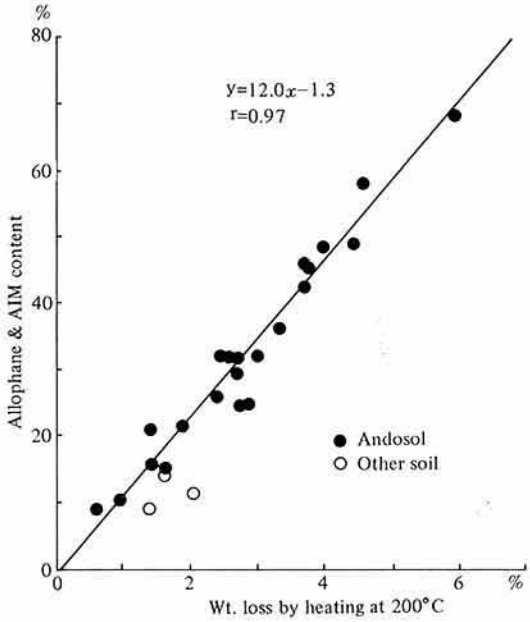

Fig. 3. Correlation between allophane and AIM contents, obtained from alternate dissolution with HCl and NaOH solution, and weight loss by heating at 200°C.

Table 2. Degree of decomposition of organic materials with reaction of H_2O_2 solution, and its effect to weight loss by heating at 200°C

Sample		Original soil	Decomposed with acid H_2O_2 solution	Decomposed with alkaline H_2O_2 solution
21-1	Total-C (%)	7.59	1.19	0.26
	Weight loss at 200°C (%)	5.92	3.70	2.85
29-1	Total-C (%)	4.20	0.63	0.17
	Weight loss at 200°C (%)	4.49	2.75	1.40
IN15-1	Total-C (%)	8.57	1.79	0.29
	Weight loss at 200°C (%)	9.03	6.50	3.95
32-1	Total-C (%)	12.08	1.57	0.27
	Weight loss at 200°C (%)	6.19	3.40	2.06

Based on 105°C-dried weight.

heating at 200°C is generalized as follows: The allophane and AIM contents, y, are calculated on the basis of the weight loss by heating, x, from an equation, $y=(b/a)x$, where a is weight loss of the standard sample between 105 and 200°C, and b is the allophane and AIM contents in the standard sample measured by means of the alternate dissolution with 8 N HCl and 0.5 N NaOH. The standard sample must have high allophane and AIM contents, and low contents of organic materials, such as the Kanumatsuchi weathered pumice used in this study. Many of the other weathered pumices and the subsoils of andosols should be useful, accordingly.

The coexistence of organic materials influenced strongly on the weight loss by heating at 200°C as shown in Table 2. Only 79 to 87% of organic materials in the soil samples was decomposed with the acid H_2O_2 solution, while, 96 to 98% of them was volatilized with the alkaline H_2O_2 solution (Table 2). The coexistent organic materials must be removed by the procedure shown in Fig. 2, consequently. This problem is very important in using this new method for the rapid determination of allophane and AIM in soils.

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