A Rapid Method for Determining Major Constituents in Soils by X-Ray Emission Spectrometry with a Glass Beads Technique

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Introduction

In spite of the general recognition of the fact that a knowledge of the total amount of the main constituents in soils is of fundamental importance in selected fields of soil science, we seem to have only a limited amount of data, even at present. This is mainly because the "conventional wet chemical method" requires such complicated operations and skillful techniques that reliable results are obtained only when performed by well-trained analysts. Recent advances in instrumental analyses, especially those in atomic absorption spectrophotometry (AAS), have made it possible to carry out total analysis under a less strained condition. The procedures based on these techniques are, however, still too time-consuming for handling a large number of soil samples.

The method described in this report was developed in our laboratory by a combination of X-ray emission spectrometry and a glass beads technique. Though the method has an obvious disadvantage that the instrument (X-ray spectrometer plus high frequency heating furnace) is somewhat too expensive, it can provide a rapid and reliable method for total analysis of soils for non-specialists as a result

of highly automated procedures. More than 3,500 samples of soils and related materials have been successfully analyzed by this method in these 5 years.

Wet chemical methods

It is obvious that the usability of the X-ray method cannot be fully evaluated until the chemical methods employed for the purpose of comparison are proved to be highly reliable. It seems essential, therefore, to briefly refer to the chemical procedures, though their details were frequently altered to accommodate to newly developed instruments and techniques.

1) Decomposition of samples and analytical methods

The procedures described below are mainly for soils of average composition. Many soil samples having wide range of chemical composition were decomposed and analyzed. The amount of acids and the ratio of dilution must be changed according to the elemental composition of samples. Fine grinding of sample prior to chemical treatment proved to be an essential step to materialize the complete dissolution as well as to avoid errors caused by sample inhomogeneity.

(1) Acid digestion method: 1.000 g of sample was treated with 10 ml of $HClO_4$–HNO_3 (1 : 1 mixture) to destroy the organic matter in soils and then twice with 15 ml of

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HClO$_4$–HF (1 : 2 mixture) in a tefron beaker on a hot plate. When the sample is free from organic matter, it is possible to skip the HClO$_4$–HNO$_3$ treatment. The residue was heated with 5 ml of HCl (20%) and then dissolved by adding 30–50 ml of H$_2$O with gentle boiling and finally made up to 100 ml. No significant change in the concentration of the major constituents was observed for 1 year or more when the solution was stored in a polypropylene bottle.

The solution was then analyzed for Na, Mg, K, Ca, Mn, and Fe by AAS after a 10–100 fold dilution. Interference due to Al on Mg and Ca was suppressed by the addition of Sr (5,000 ppm). Aluminum was always determined by using a N$_2$O–C$_2$H$_2$ flame and so was Ca when the interference of Al was too severe to control by the addition of Sr. Phosphorus and Ti were determined by spectrophotometry after the color development with vanadomolybdate and diantipyrylmethane respectively. Although a little less sensitive than tiron, the most widely used reagent for Ti, diantipyrylmethane is less subject to interference from other metallic ions and to variation of acid strength of the solution.[4]

(2) Fusion method: 0.500 g of sample was fused with 2 g of Na$_2$CO$_3$–H$_3$BO$_3$ (10 : 1 mixture) in a Pt dish. The melt was dissolved in HCl (20%) and the most parts of SiO$_2$ were coagulated with polyethylene oxide and filtered off.[2] This method enables us to eliminate the tedious dehydration procedure of SiO$_2$. The separated SiO$_2$ was first ignited, and then heated with a mixture of H$_2$SO$_4$ and HF. The loss in weight due to the treatment with H$_2$SO$_4$–HF was regarded as the main Si. A small fraction of Si still remaining in the filtrate was determined by spectrophotometry.

2) Reliability of chemical analysis

Fig. 1 shows the summarized results of JB–1 and JG–1, the rock standards provided by Geological Survey of Japan.[1] The length of the bars represents the magnitude of standard deviation. The thick and thin lines respectively show the reported values and the averages of this experiment. Figures shown on each side of the bars are relative standard deviation, RSD, of the repeated determinations. Number of repetition was 3 for SiO$_2$ and 10 for the other constituents.

Relative standard deviation was 0.1–1.5% and the difference between the reported value and our result was smaller than the standard deviation of the reported value for all of the constituents. The above results indicate that the precision and accuracy of the method employed in our laboratory are as good as or even better than other procedures used elsewhere and/or adopted formerly. Analytical results of other 7 rock standards (data was not presented here) were also quite satisfactory, though the accuracy seems to be somewhat poorer than that presented in Fig. 1.

X-ray analysis

The procedure described here was adopted as a compromise of various contradictory factors affecting the precision and accuracy of the determination.

1) Preparation of glass beads

For this purpose, a specially designed dish made of what is known as "non-wet alloy" (95% of Pt and 5% of Au) was used. This type of alloy is hardly wetted by borate fusion mixture and therefore, cleaning is made much easier or unnecessary.

A finely powdered sample (0.500 g) and 4.500 g of Na$_2$B$_4$O$_7$ (provided by Merck Corp. for the flux in X-ray emission analysis) were thoroughly mixed in the dish with a plastic spoon, trying not to scratch the inner surface. The total weight of the dish, sample, and the flux was recorded. The contents in the dish were fused in a high frequency heating furnace at about 1,100°C for 4 min and 20 sec. A preliminary heating was necessary, without covering the dish, to ensure enough air supply for samples containing higher amount of organic matter. The dish was kept still for the first 2 min and then tilted from side to side for the latter 2 min to remove the bubbles formed during the decomposition
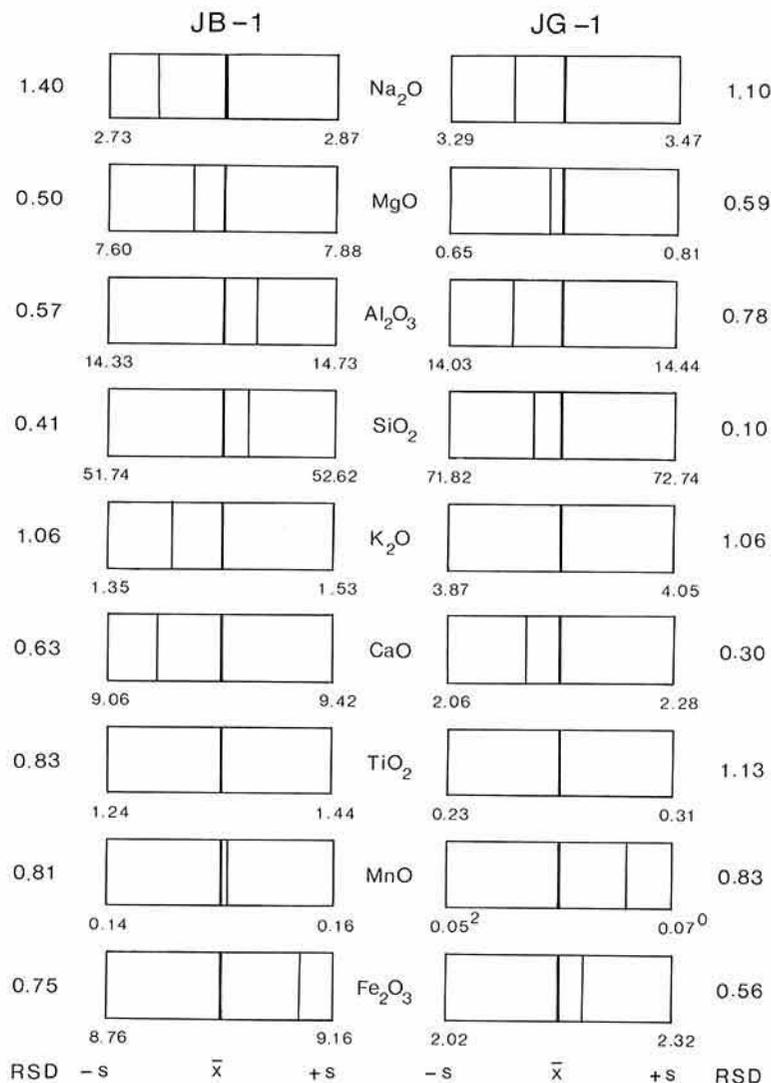
Fig. 1. Summary of data on JB–1 and JG–1 analyses

of samples, and finally kept horizontally again for the last 20 sec to obtain a glass bead of uniform thickness. All of these steps proceed automatically according to the programed sequences.

After cooling, the weight of the dish containing the glass bead was measured and the flux was added to the glass bead until the total became equal to the previously recorded value. Addition of a slight excess of the flux (5–10 mg) is recommended to compensate losses during the second fusion. The glass

bead and the flux were fused again by exactly the same procedure as described above. The melts were solidified in the dish to avoid possible contamination and for ease of operation. In most cases, the weight of the beads fall within 5.00 ± 0.01 g. The glass beads thus formed are easily removed from the dish by a gentle bumping of the dish against the bench. Repeatability and reproducibility of the above sample preparation was presented earlier.[9]

2) Construction of the calibration curve

Twelve rock standards were used to obtain the calibration curve for each constituents. These are AGV-1, BCR-1, G-2, GSP-1, and PCC-1 provided by U.S. Geological Survey,[3] BR, GA, Mica-Fe, and Mica-Mg provided by Centre de Recherches Pédrographique et Géochimiques,[3] and JB-1 and JG-1. In addition to the regular 10-fold dilution, a 20-fold dilution was also carried out to widen the concentration range of the calibration curve. AGV-1 was used as a reference specimen and X-ray intensity ratio was employed instead of X-ray intensity itself for calculating the slope and the intercept of the calibration curve to avoid errors due to instrumental drift. The concentrations of the main constituents in soils usually fall within the concentration range of the calibration curves with the exception of Al_2O_3 in soils of high clay contents, SiO_2 in some sandy soils, and MnO in some paddy soils.

3) Correction of matrix effects

The calibration curve thus obtained showed a good linearity for each constituent, but statistical analyses revealed that calibration curves prepared with different kinds of materials such as soils, rock standards, and chemicals were slightly but significantly different each other.

This indicates that the elimination of the matrix effect was not necessarily sufficient in a 10–20 fold dilution. But it was found possible to overcome this problem when the above effect, which is due to the difference in the elemental composition of samples, was compensated by dividing the concentration by the ratio of the mass-absorption coefficient value of the matrix. This compensated concentration is termed the "apparent concentration" in this report.

4) Conversion of X-ray intensity to concentration

First, the apparent concentration was estimated from X-ray intensity ratio by the use of the calibration curve obtained by the above procedure. Then, this value was converted to concentration by computation. The computation method employed in this experiment is essentially similar to that proposed by Vanden Heuvel,[6] but modified so as to accomplish an easier and faster computation by using a programable desk top calculator, or more preferably by means of a computer. A more dfetailed description of the method was presented elsewhere.[8]

Comparison of two methods

The values obtained by the chemical and X-ray method were examined for Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, MnO, and Fe_2O_3 and were summarized in Fig. 2. The concentrations of these constituents are expressed on the air dry matter basis.

Agreement of the two methods was highest in SiO_2 and lowest in P_2O_5. The slopes of the regression lines were very close to unity and the intercepts were negligibly small with the exception of P_2O_5. This excellent agreement of the two methods is of great practical importance since a considerable part of the X-ray analysis was conducted by untrained workers. While the correlation coefficient was more than 0.99 in P_2O_5, the regression line apparently deviated from the 1 : 1 line (the line of the perfect correlation). This may be attributed to the lower X-ray intensity of P_2O_5. In spite of this poor result, this method seems to be still of some use in soil analysis to a certain extent. In K_2O, the regression line was practically identical with the 1 : 1 line, but the correlation coefficient was somewhat lower than the other constituents. However, such a greater scattering of K_2O seems to be insignificant for soil analysis in most cases.

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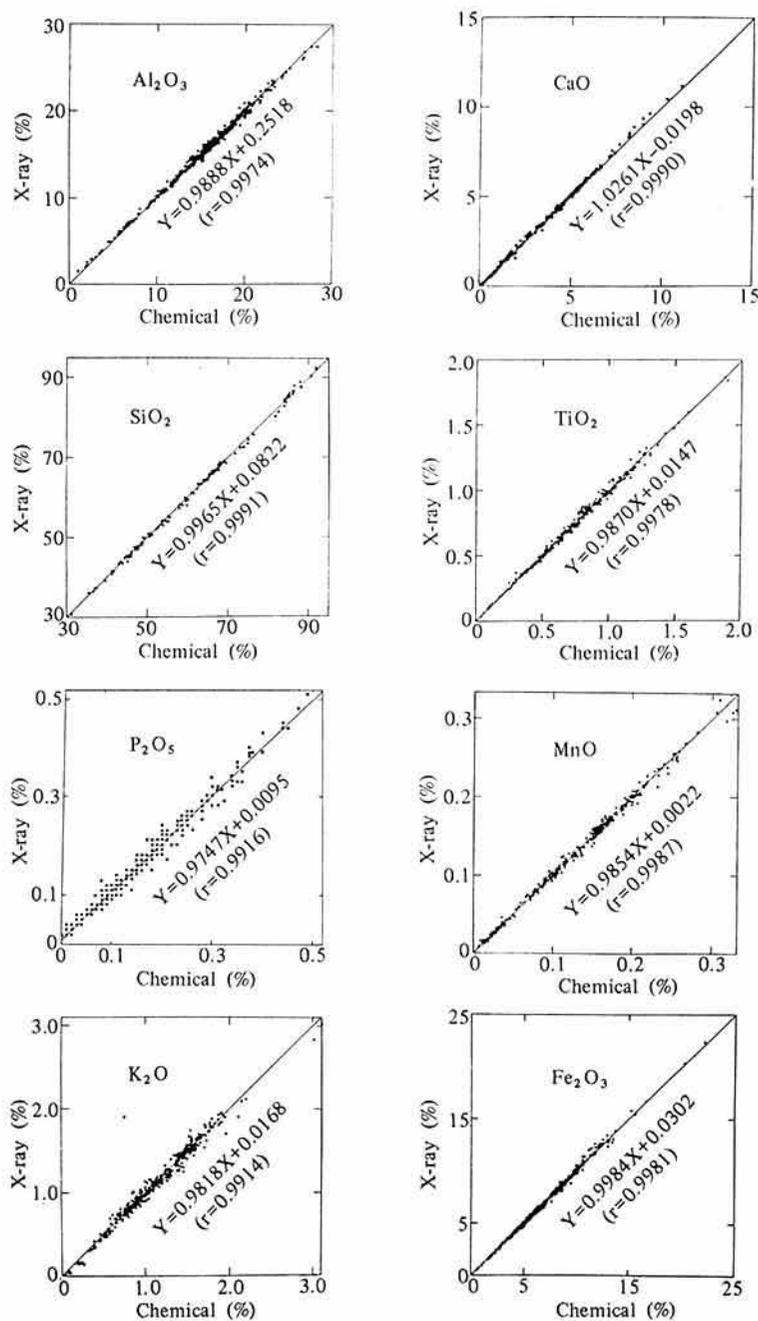
Fig. 2.   Results of X-ray analysis as compared with
those of chemical methods

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