

Spectrophotometric Determination of Soil Chemical Properties Using Soiltek® KA-P Spectrophotometer

Hae-Nam Hyun*, Sang-Sil Oh**, Bon-Jun Koo*** and Ho-Jun Kang****

ABSTRACT

To enable rapid and convenient soil test, new soil analytical methods, which require only one instrument, UV/Vis spectrophotometer, were developed and named "Soiltek KA-P spectrophotometric methods". The Soiltek® KA-P spectrophotometric method was compared with standard method of RDA in analytical capability for soil chemical properties. Using the 78 soils collected from upland, paddy, orchard, and vinyl house soils, soil organic matter, exchangeable K, Ca, and Mg, CEC, available SiO₂, and nitrate were analyzed by the two methods. The color stability (ratio of the absorbance at elapsed time *t* to the absorbance at time *t*=0) of organic matter, Ca, Mg, and available SiO₂ decreased to about 2% within one hour. However, that of exchangeable K, CEC, and nitrate remained constant. The results obtained with Soiltek® KA-P spectrophotometric method showed highly significant correlation with those measured by the standard method of RDA ($R^2 > 0.9501$), in which the slopes were near unity of 1.0 ± 0.05 . The standard deviation values of organic matter, exchangeable K, Ca, and Mg, CEC, available SiO₂, and nitrate were apparently lower than $\pm 1.8 \text{ g kg}^{-1}$, $\pm 0.05 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 0.18 \text{ cmol}^+ \text{ kg}^{-1}$, and $\pm 0.13 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 1.0 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 5.0 \text{ mg kg}^{-1}$, and $\pm 10.0 \text{ mg kg}^{-1}$, respectively. All the measurements showed coefficients of variation of less than 7~17% and were within the confidence level of 95%, which means both the methods are precise. Considering the relative simplicity, low cost, precision and accuracy, the proposed Soiltek® KA-P spectrophotometric methods could be recommended as an alternative to standard method.

Key words: Soil analysis, Soiltek KA-P spectrophotometric method, Standard method of RDA, Soil components.

Introduction

A rapid soil test is prerequisite for the fast fertilizer recommendation. However, standard methods for soil test used in Korea are time-consuming, and require several equipments, such as spectrophotometer for nitrate, available phosphate and silicate, atomic absorption spectrophotometer for exchangeable K, Ca, and Mg,

titration apparatus for soil organic matter, and Kjeldahl distillation apparatus for CEC. Moreover, for the CEC analysis, complex procedures such as saturating, washing, and extracting steps are required.

Therefore, it is necessary to develop new analytical methods having simple procedure and using only one instrument for fast and convenient soil test without damaging accuracy compared with RDA methods. Soiltek®

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KA-P spectrophotometer which is one-touch operation type of soil analyzer was developed to determine soil components for fertilizer recommendation (Hyun et al, 1999). Spectrophotometric methods are more often used because of their simplicity and low cost.

Spectrophotometric techniques were applied to measure soil organic matter contents (Sims and Haby, 1971; De Bolt, 1974), K in leaf (Tubino and Torres, 1992) and fertilizer (Jain and Sarkar, 1976), Ca in paper machine white water (Nyman and Ivaska, 1995), water, urine, pharmaceutical samples (van Staden and Taljaard, 1996), serum, and wastewater (Hansen et al, 1978; Rocha et al. 1998), and Mg in water (Mann and Yoe, 1956; Mann and Yoe, 1957) and soil extract (Peaslee, 1966).

Based on the above methods or principles, in this study more convenient and rapid methods using Soiltek® KA-P spectrophotometer were designed for the analysis of organic matter, exchangeable K, Ca, and Mg, cation exchange capacity, available SiO₂, and nitrate in soils. Results from new methods were statistically compared with those from conventional standard methods of RDA.

Materials and Methods

1. Soil samples

The 78 surface soil samples were collected from upland, paddy, orchard, and vinyl house soils to cover various land-uses. The soil samples were air-dried and crushed to pass 2 mm sieves. Among them, 56 soils were used for analyzing organic matter, exchangeable K, Ca, and Mg, and CEC, 32 paddy soils for available SiO₂, and 28 soils from upland and vinyl house for nitrate.

2. Methods

Soil organic matter

Walkley-Black method was used for organic matter as a standard method, while Soiltek® KA-P spectrophotometric method was modified by changing concentration and

reducing reagents for simple preparation from the methods proposed by Sims and Haby (1971) and De Bolt (1974).

Nitrate

After extracting from soils with 2M KCl solution, nitrate was determined by Brucine method as a standard method. It was compared with Soiltek® KA-P spectrophotometric method which was made from the modification of UV spectrophotometric screening method (APHA, 1998)

Exchangeable K, Ca, and Mg

Exchangeable Ca and Mg in solution extracted with 1M ammonium acetate and exchangeable K with sodium acetate buffer solution were analyzed by atomic absorption spectrophotometer (Varian Spectra AA 220). In Soiltek® KA-P spectrophotometric method using an aliquot of the extracted solution, exchangeable Ca was determined after modifying the method proposed by Nyman and Ivaska (1995), van Staden and Taljaard (1996), Hansen et al (1978), Rocha et al (1998), and Oguma et al (1985). Using another aliquot of the same extracted solution, exchangeable Mg was determined after modifying the method proposed by Mann and Yoe (1956), Mann and Yoe (1957), and Peaslee (1966). Exchangeable K was determined by modifying the method proposed by Cox et al. (1999), Torres and Tubino (1994), Tubino and Torres (1992). The modification was mainly performed by changing the concentration and the way of mixing or adding reagents for Ca and K.

Available SiO₂

After being extracted from soils with 1M sodium acetate solution, available SiO₂ in the solution was determined by the RDA standard method (RDA, 1988). Soiltek® KA-P spectrophotometric method modified from the RDA standard method was used for the determination of available SiO₂ contained in the same solution.

Cation exchange capacity

Determination of CEC in standard method was performed by three steps of saturating with ammonium, removing the excessively saturated solution, and replacing with acidified NaCl solution. After making copper or methylene blue be adsorbed on the soils, remaining copper or methylene blue concentration in solution was measured using Soiltek® KA-P spectrophotometer, then the CEC was calculated by the adsorbed amount (Yang, 2000; Hyun et al, 2000).

3. Analytical Procedure

Detailed experimental procedures referred to the user manual of Soiltek KA-P spectrophotometer (Hanson Co. Ltd, 1999). All measurements were performed in triplicate. To evaluate the accuracy of the Soiltek® KA-P spectrophotometric methods proposed in this study, the means, standard deviations, and coefficients of variation were compared with those of the standard methods.

Results and Discussions

1. Spectrum characteristics of color developing reagent

The color development occurred usually within ten minutes after mixing samples and color developing reagents during determination of all the soil chemical properties. Each reaction mixture for each soil chemical properties was scanned from 340 to 850 nm to obtain the maximum absorbance difference between the sample and blank as a control. In case of nitrate measurement, UV regions were applied. Each wavelength displayed maximum differences was used as an optimum wavelength for the determination of each soil chemical properties.

Organic matter

When the oxidizing reagents for soil organic matter were added to soil or deionized water, the obtained spectra were

shown in Fig. 1a. The maximum difference in absorbance between soil organic matter and deionized water in the presence of oxidizing reagent lied at 595 nm (Fig. 1b), at which the interference could be avoided.

Exchangeable K

Exchangeable K was measured using the turbidimetric principle. The longer the wavelength the lower the absorbance was detected. The wavelength range of 300~800nm could be used. However, considering the absorbance stability, the optimum wavelength was selected at 690nm (Fig. 2a, b).

Exchangeable Ca

When phthalein purple as a color developing reagent was added to extracting solution in the presence of Ca, one peak maxima was observed at 573 nm. Even though there was a little interference to ammonium acetate solution in the

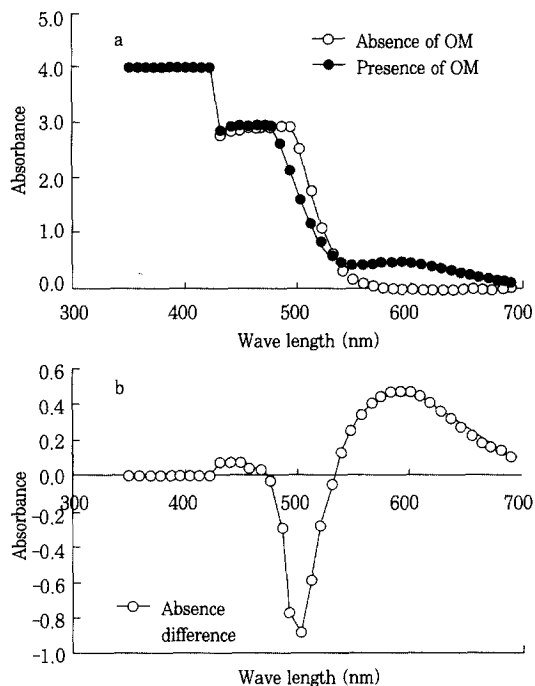


Fig. 1. Spectra for oxidizing solution and organic matter (a) and their absorbance differences (b).

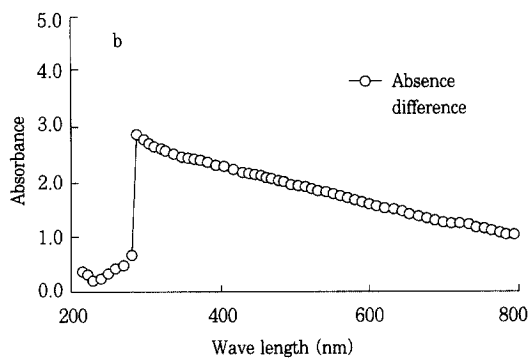
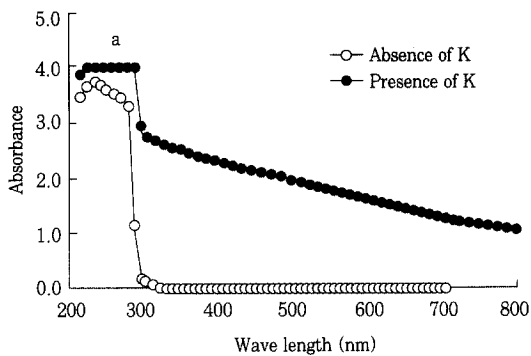


Fig. 2. Spectra for potassium color developing reagent in the absence or presence of K in sodium acetate solution(a) and their absorbance differences(b).

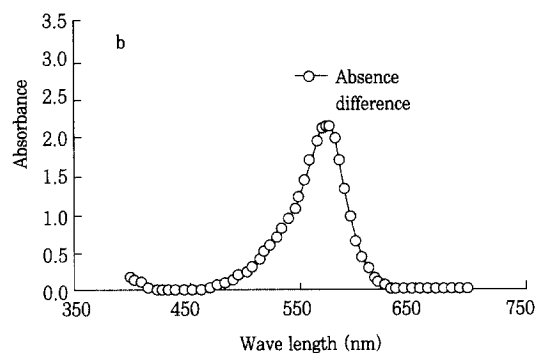
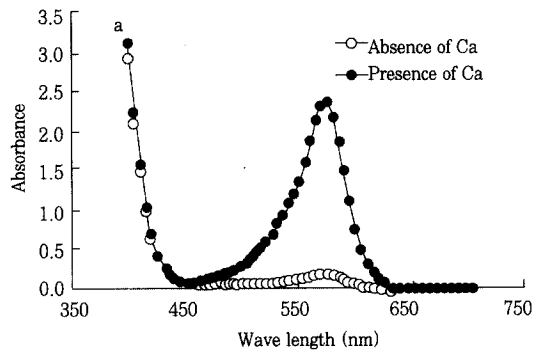


Fig. 3. Spectra of calcium color developing reagent in the absence or presence of Ca in ammonium acetate solution(a) and their absorbance differences(b).

absence of Ca, the optimum wavelength was selected at 573nm(Fig. 3a, b).

Exchangeable Mg

In the presence of Mg, two maxima were observed at 530 and 550nm, while in the absence of Mg, the maximum absorbance was observed at 600nm. Accordingly, the maximum difference in absorbance between the presence and absence of Mg was at 515nm, which is different from the absorbance of 505nm that Mann and Yoe(1957) reported, although the shape was the same as shown in Fig. 4.

Cation Exchangeable Capacity

There are always sufficient cations held by electrostatic forces on soil particle surfaces to balance the surface

negative charge known as the cation exchange capacity, or CEC. The cations commonly held in this way are calcium, magnesium, potassium, and ammonium, with increasing amounts of sodium in saline soils, and hydrogen and aluminium in acid soils. These cations are readily exchangeable with copper, because copper ions can be more strongly adsorbed than the previous cations. In addition, copper compounds in solution has an absorbance in visible region of spectra(Fig. 5), while the size of absorbance varies depending on the copper concentration. Therefore, CEC was spectrometrically obtained by measuring the decrease in absorbance using a single-point adsorption of copper. The absorbance of adsorbing solution increased gradually from 590nm and showed the maximum at 830nm. However, considering the measuring

convenience, the optimum absorbance was specified at 720nm.

2M KCl extractable NO₃

Measurement of UV absorption at 220nm enables rapid determination of nitrate(APHA, 1998). However, because of a large amount of dissolved organic matter in 2M KCl extracted solution, two peak maxima were observed at 220 and 275nm(Fig. 6a). When organic matter removing reagent(Hanson Tech., 1999) was added in order to remove the interference, the maximum absorbance was shown at 214nm(Fig. 6b).

Available SiO₂

As shown in Fig. 7, there was no spectral interference in

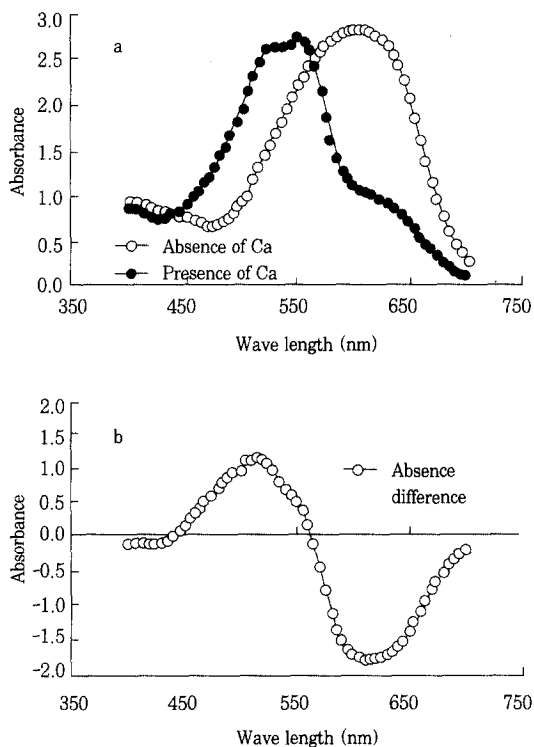


Fig. 4. Spectra of magnesium color developing reagent in the absence or presence of Mg in ammonium acetate solution(a) and their absorbance differences(b).

sodium acetate extracting solution. The absorbance of silicate solution increased gradually from 400nm to 770nm, while the increase in absorbance was relatively low between 600 and 700nm. The optimum wavelength for

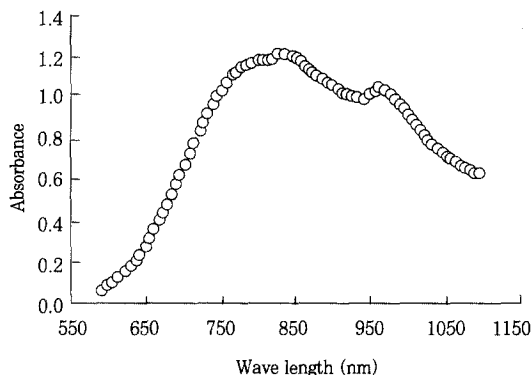


Fig. 5. Spectra of the adsorbing solution for the determination of cation exchange capacity.

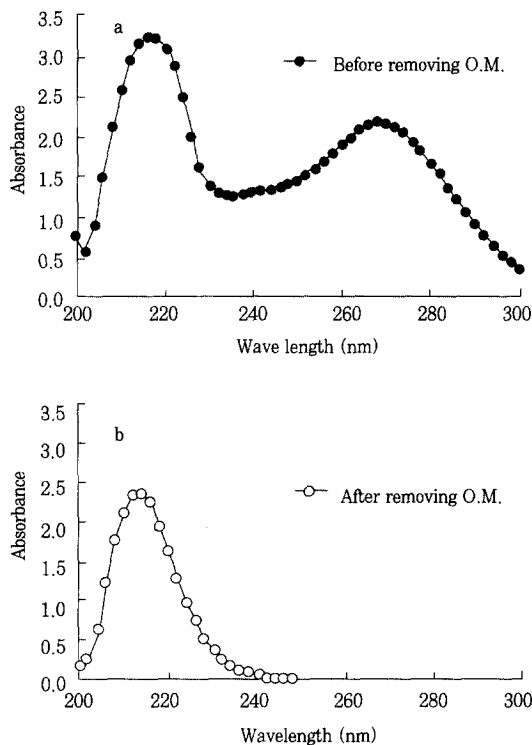


Fig. 6. Spectra for KCl extractable NO₃ before(a) and after removing organic matter(b).

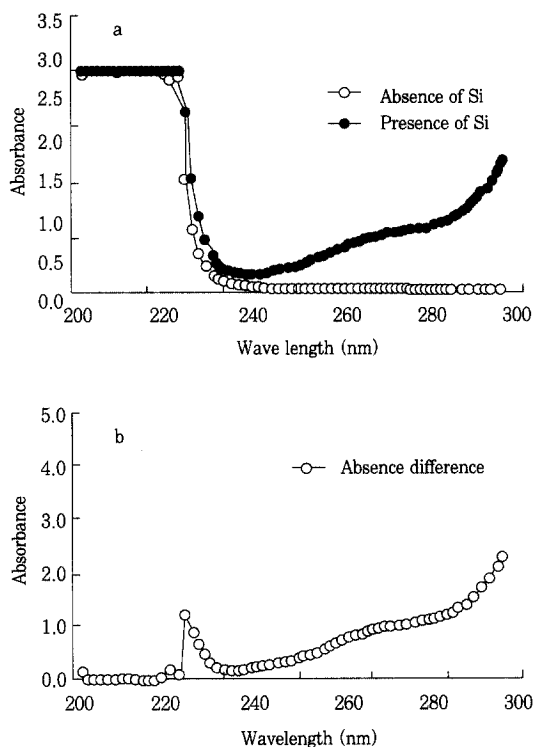


Fig. 7. Spectra of SiO₂ color developing reagent in the absence or presence of Si in sodium acetate solution(a) and their absorbance differences(b).

measurement of silicate was specified at 650nm in which the variance was low.

2. Color stability

The color stability against the time seemed to be excellent from 10 to 60 minutes as shown in Fig. 8. That of organic matter, Ca, Mg, and SiO₂ decreased to about 2% with time elapsed, presumably because of precipitation of colloidal particles by allowing to stand. However, exchangeable K, CEC, and nitrate remained constant. This means the manipulations can be comfortably done in that time period. When the extent and time was given, the color for CEC and nitrate still remained constant upto one day.

3. Correlation, precision, and accuracy

The results of soil chemical properties by the Soiltek® KA-

P spectrophotometric methods showed highly significant correlation with those measured by the standard method ($R^2 > 0.9501$), in which the slopes were near unity of 1.0 ± 0.05 (Fig. 9). It indicates that the proposed new method could be accurate and rather practical to use because of convenience and simplicity compared with standard methods.

The standard deviation of obtained results for organic matter, exchangeable K, Ca, and Mg, CEC, available SiO₂, and nitrate were apparently lower than $\pm 1.8 \text{ g kg}^{-1}$, $\pm 0.05 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 0.18 \text{ cmol}^+ \text{ kg}^{-1}$, and $\pm 0.13 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 1.0 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 5.0 \text{ mg kg}^{-1}$, and $\pm 10.0 \text{ mg kg}^{-1}$, respectively (Fig. 10). All the measurements were within the confidence level of 95%, which means that both methods are precise.

The precision, represented as the coefficients of variation which is percentage of standard deviation against the mean of each component for all the soils was shown in Fig. 11. The coefficients of variation were less than 7~17% depending on components. However, the tendency was observed that the lower the concentration was the higher the coefficients of variation were, as reported in the spectrophotometric determination of Mg (Mann and Yoe, 1956).

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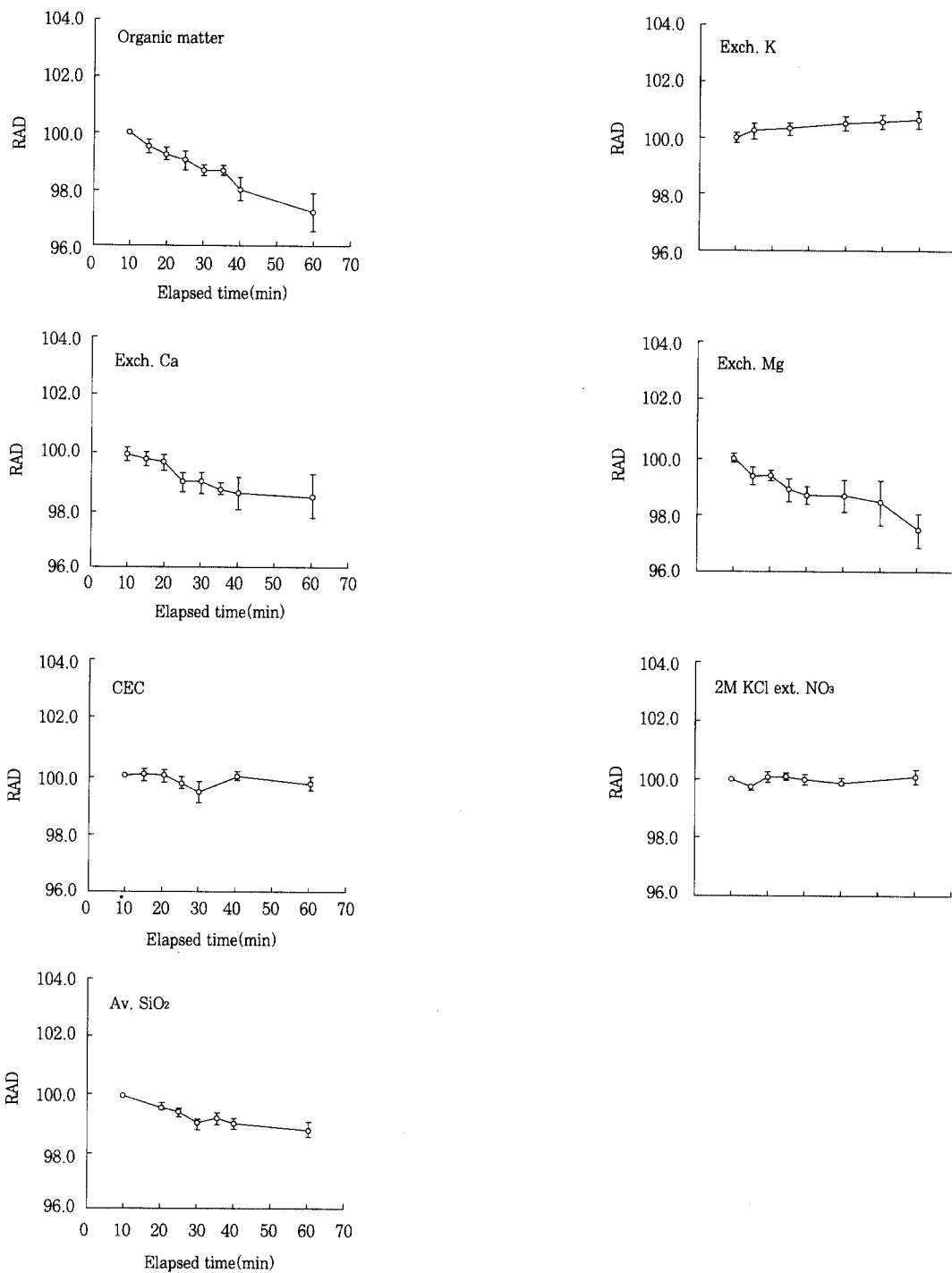


Fig. 8. Relative absorbance deviation(RAD) which is obtained by dividing the absorbance at elapsed time t by the absorbance at time t=0 and multiplying by 100.

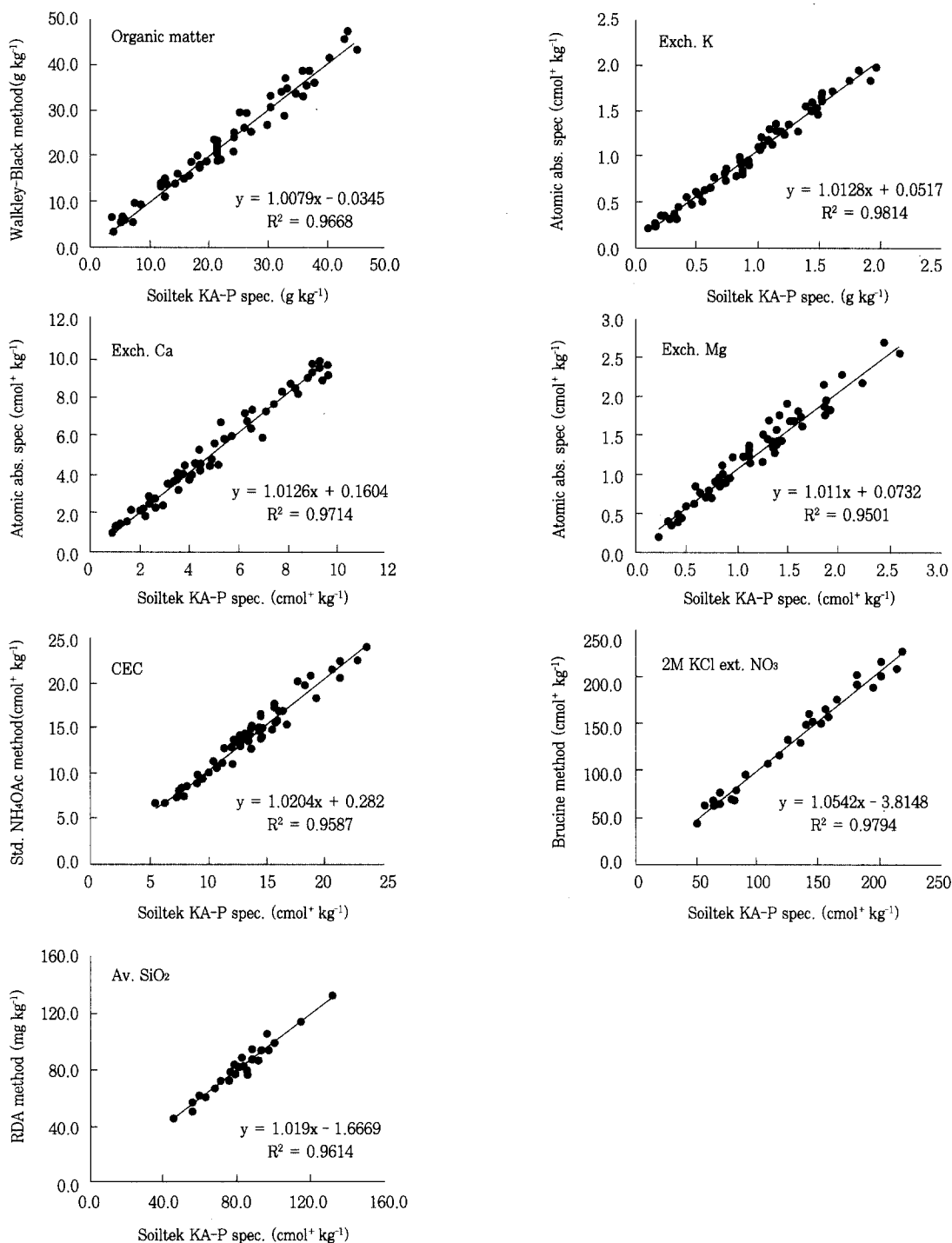


Fig. 9. Linearity between Soiltek KA-P spectrophotometric method and standard method.

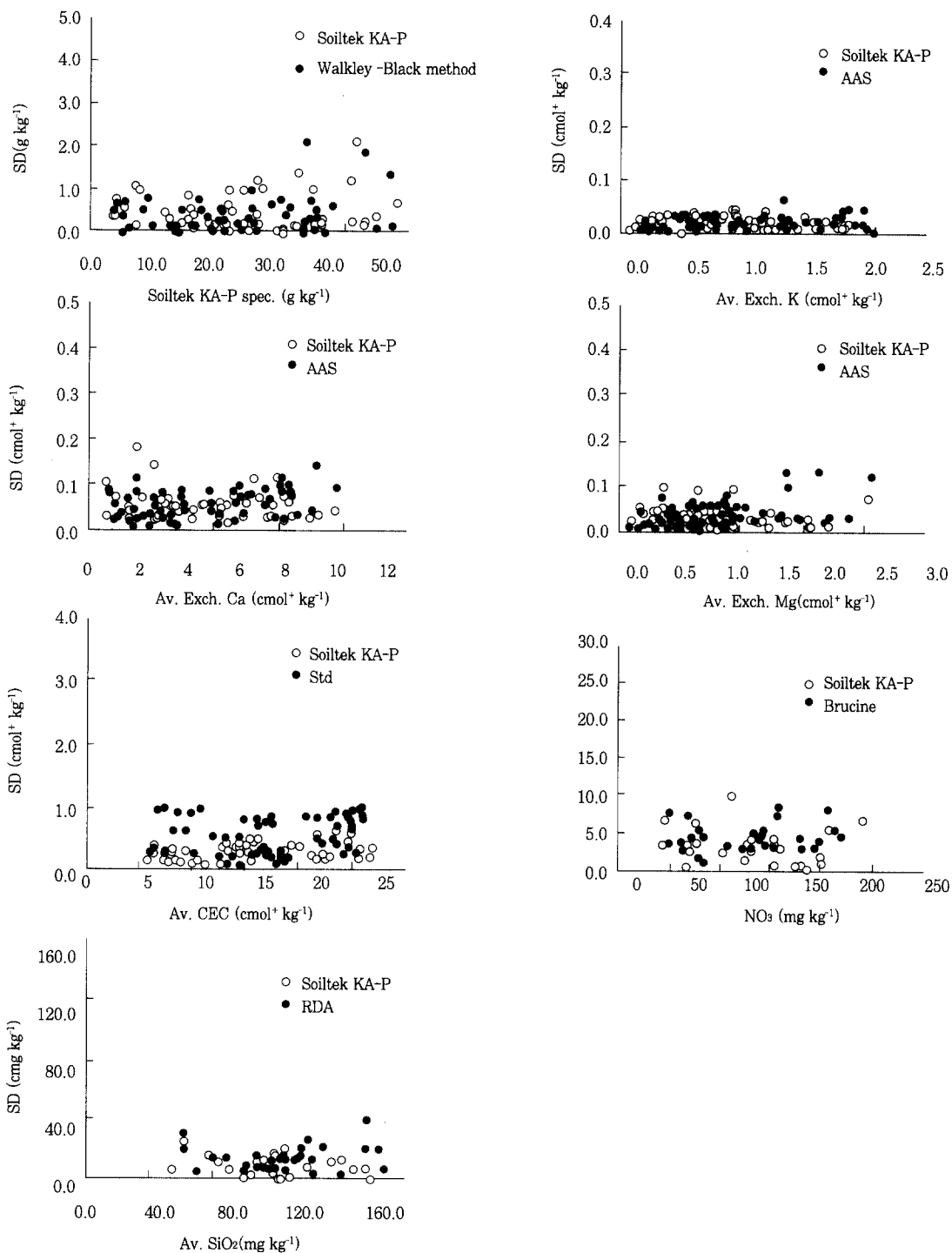


Fig. 10. Standard deviations for Soiltek KA-P spectrophotometric method and standard method.

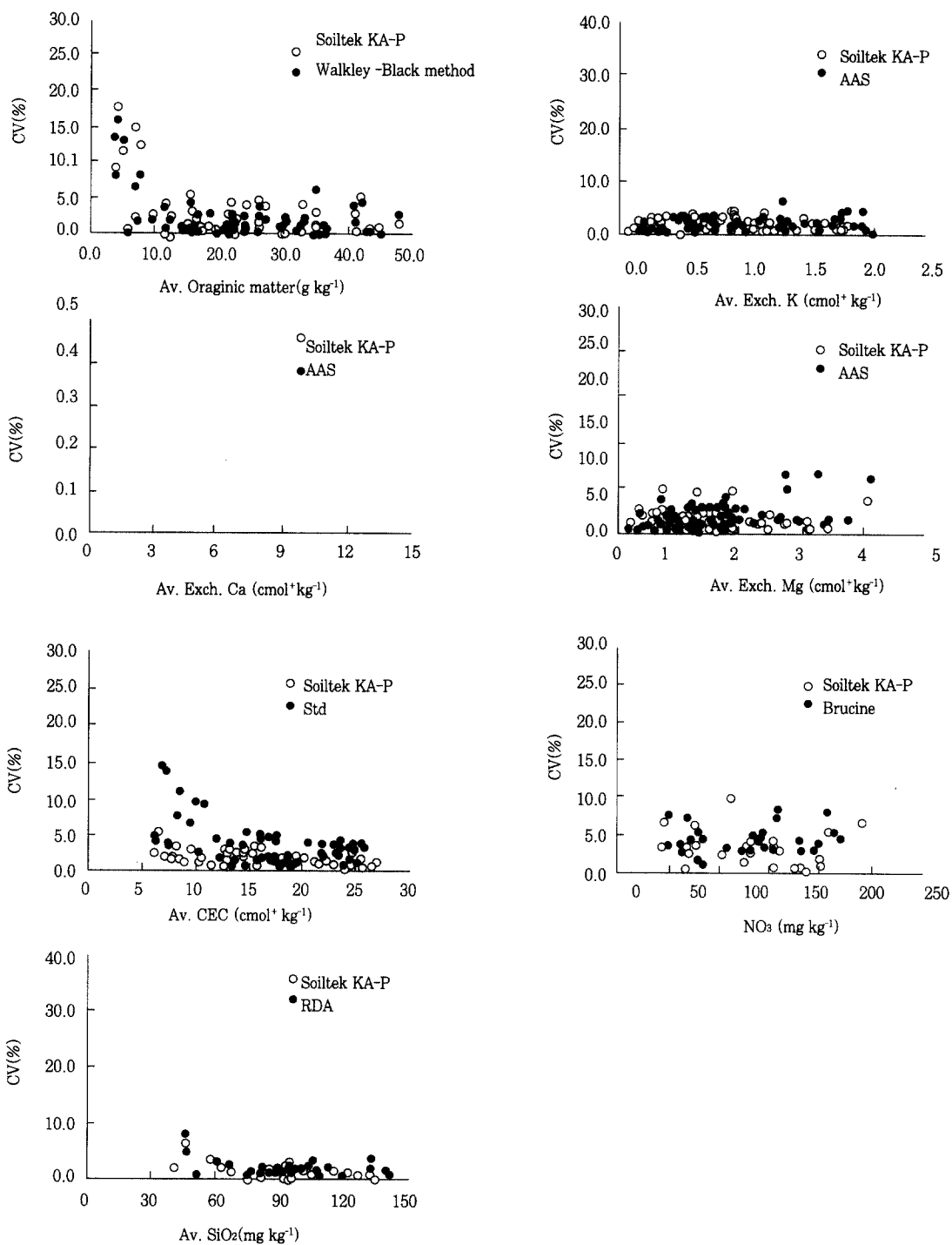


Fig. 11. Coefficients of variation for Soiltek KA-P spectrophotometric method and standard method.

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Soiltek KA-P 분광광도계를 사용한 토양 화학적 성질의 분광학적 분석

현해남* · 오상실** · 구분준*** · 강호준****

일반 밭, 논, 과수원 및 비닐하우스 토양 78점을 채취하여 3반복으로 농촌진흥청 표준분석법과 Soiltek® KA-P 분광광도계법으로 유기물, 치환성 K, Ca 및 Mg, CEC, 유효규산 및 질산염 함량을 측정하였다. Soiltek® KA-P 분광광도계로 측정된 유기물, 치환성 Ca, 및 Mg 용액의 발색 안정도는 1시간 동안 약 2% 정도 낮아졌으며, 치환성 K, CEC 및 질산염은 거의 변화가 없었다. Soiltek® KA-P 분광광도계로 측정된 분석 절대값은 농촌진흥청 표준분석법으로 측정된 값과 거의 1:1의 관계를 갖고 있었으며, 결정계수(R²)는 0.9501 이상이었다. 두 방법으로 측정된 유기물, 치환성 K, Ca 및 Mg, CEC, 유효규산 및 질산염의 표준편

차는 각각 $\pm 1.8 \text{ g kg}^{-1}$, $\pm 0.05 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 0.18 \text{ cmol}^+ \text{ kg}^{-1}$ 및 $\pm 0.13 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 1.0 \text{ cmol}^+ \text{ kg}^{-1}$, $\pm 5.0 \text{ mg kg}^{-1}$ 및 $\pm 10.0 \text{ mg kg}^{-1}$ 이하였다. 모든 성분에 대한 분석값은 95% 신뢰수준을 만족시켰으며, 변이계수는 7~17% 이하였다. 따라서, 기기조작의 간편성, 저가 기기의 사용, 정확도, 정밀도 등을 고려한다면 Soiltek® KA-P 분광광도계에서 제시하는 방법으로 측정하는 것도 유용한 방법이라고 생각된다.

Key words: Soil analysis, Soiltek KA-P spectrophotometric method, Standard method of RDA, Soil components.

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