Simplified Analysis for Soil Samples with Compact Water Quality Meter <LAQUAtwin>

– Measurement of exchangeable calcium ion and potassium ion in soil –

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Exchangeable calcium ion (Ca^{2+}) and potassium ion (K^+) extracted with 1 mol/L ammonium acetate (NH_4OAc) solution were measured with Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Simple and quick measurements by AAS or ICP-OES are difficult in the field because these are large analytical instruments. A simplified analysis was tried with the compact water quality meter <LAQUAtwin> (Ion Selective Electrode; ISE). In case of measurement of Ca^{2+} and K^+ with ISE methods, the high NH_4OAc concentration solution produced inaccurate results due to a potential difference shift. In this report, LAQUAtwin meters are used for soil sample measurements. The procedure used herein proves that Ca^{2+} and K^+ are easily measurable using this procedure with the ISE methodology.

Introduction

In agriculture, a soil test is necessitated to maintain suitable soil environment for crop growth. A soil test is the analysis of soil samples to determine chemical properties such as the amount of nutrient contained in soil and physical properties such as soil hardness or permeability. Chemical properties are generally pH, electric conductivity and nutrient concentration (nitrogen, phosphorus, potassium, calcium, magnesium etc.). Potassium, calcium, and magnesium (basic cations) exhibit mutual antagonism on absorption to crops, so it is necessary to keep adequate ratio of these elements. Also, the results of analysis for potassium, calcium, and magnesium are used to calculate the base saturation as the indicator of adequate soil condition for planted crops. The base saturation is a proportion of base elements to the Cation Exchange Capacity (CEC) signifying the maximum quantity of total cations that a soil is capable of holding. The extractable base elements of soil with an ammonium acetate solution can be determined by Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). In reality, the soil analysis is usually requested to an external laboratory because these instruments are not portable in the field and their operations require the expertise. Therefore, in the case of the fertilizer management on a routine basis, it is expected that requesting analysis is expensive and it takes time to get the results. On the other hand, if the results of analysis can be quickly, simply, and accurately obtained on a production field, it will enable suitable soil fertilization in real time. In fact, soil test kits allowing simple measurements without specialized knowledge and skills are available on the market. And most of their kits are based on colorimetric method and turbidimetric method. their kits provide the value determined by visual judgment with standard chart or the numerical value determined by compact chromatometer and reflectometer.

Compact Water Quality Meter <LAQUAtwin>

Compact water quality meters, LAQUAtwin, were released by HORIBA, Ltd. last year. Figure 1 shows that LAQUAtwin lineup has measurement of 7 items, pH, conductivity, sodium ion, potassium ion, nitrate ion, calcium ion and salinity. All LAQUAtwin meters are based on electrochemical sensor, namely, pH meter, conductivity meter, and ion and salt (salinity) meters, utilizing glass electrode method, 2-AC bipolar method, and Ion Selective Electrode (ISE) method, respectively. Therefore, these meters are the same as principle of electrodes for laboratory use (see Figure 2). LAQUAtwin meter is the meter integrated with sensor, and moreover, that is small enough to carry in one hand. So LAQUAtwin meter have the concept that a laboratory can be taken easily in the open air. pH, conductivity, and nitrate ion compact meters have been available before the launch of “LAQUAtwin”. These meters have been already featured as one of easy soil test tools. This report shows simple analysis of exchangeable potassium ion and exchangeable calcium ion in soil samples by using LAQUAtwin potassium ion meter and new calcium ion meter.

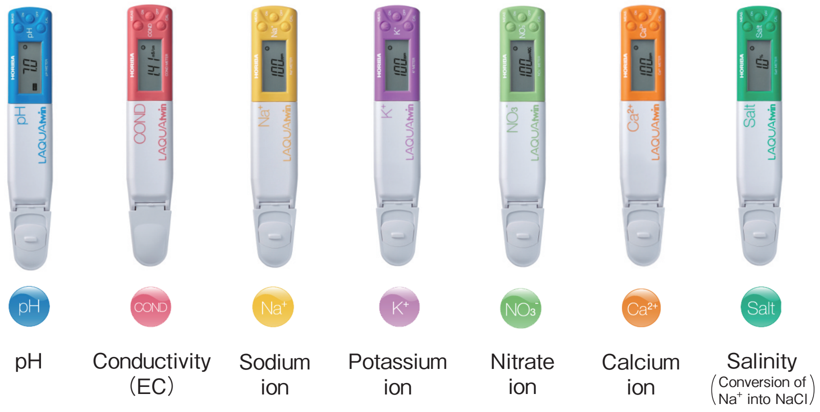

Figure 1 Appearance of Compact Water Quality meter <LAQUAtwin>.

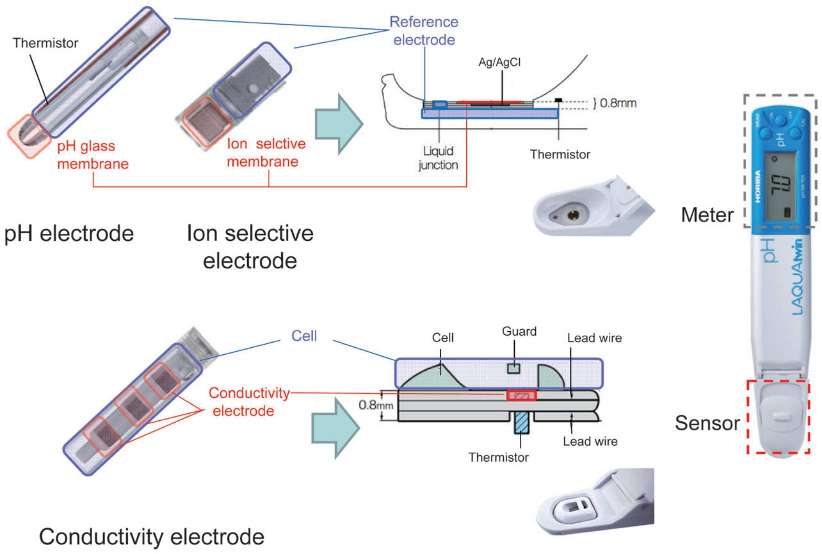

Figure 2 Diagram of LAQUAtwin flat sensors.

Experimental

Sample preparation

Each of five soil samples taken from the fields was air dried spreading on plastic tray indoor for a week, and then it was put through 2 mm opening sieve. The mixture of 5 g air dried soil and 100 mL of 1 mol/L ammonium acetate (abbreviated to NH_4OAc) solution (pH 7.0) was shaken using the reciprocal shaker in one hour (RECIPRO SHAKER SR-ⅡW, amplitude 40 m/min, speed 250 rpm). And the extraction solutions were passed through filter paper (JIS No.6) and then those solution were measured, respectively. For the measurement of potassium ions, 0.1, 0.01 and, 0.005 mol/L NH_4OAc solution in addition to 1 mol/L were prepared, and then the procedure of extraction and filtration were carried out the same as from the procedure described above.

Instruments and standard solutions

The principle of calcium ion meter (B-751) and potassium ion meter (B-731) (abbreviated to LAQUAtwinCa^{2+} meter and LAQUAtwinK^+ meter below, respectively) is the same as that of ISE method. So it is necessary to calibrate with standard solutions before the measurements by using LAQUAtwin meter. For the calibration of LAQUAtwinCa^{2+} meter, 150 and 2000 mg/L calcium ion standard solutions were prepared by the dilution with 1 mol/L NH_4OAc solution as the same concentration of extraction solution. For LAQUAtwinK^+ meter, 150 and 2000 mg/L potassium ion standard solutions were included as accessories. The two-point calibration was completed by two standard solutions for the respective meters. Also, the calcium ion and potassium ion concentrations of samples were obtained with ICP-OES (ULTIMA2, HORIBA Jobin Yvon) for comparison of the results obtained by LAQUAtwin ion meters.

Results and Discussion

Measurements of exchangeable calcium ion with LAQUAtwinCa^{2+} meter

Strictly speaking, the potential obtained by ISE method means the activity of a specific ion, (activity = [ion concentration] × activity coefficient). An activity coefficient depends on the ionic strength of a solution, and that causes measurement error. So the ionic strength of a solution need to maintain constant. Therefore, The usual procedure is that addition of indifferent electrolytes (or supporting electrolytes) which does not take part in any reactions. Standard solutions in LAQUAtwinCa^{2+} meter accessories contain 0.1 mol/L potassium chloride as supporting electrolyte that does not influence the potential measured by calcium ion sensor. However, in regard to measurement of calcium ion in soil extraction solution with ISE method, in the case of calibration with accessory standard solutions, the presence of large amount of NH_4OAc in a sample solution causes shift in the potential by the difference of ionic strength, and it is difficult to measure accurately.

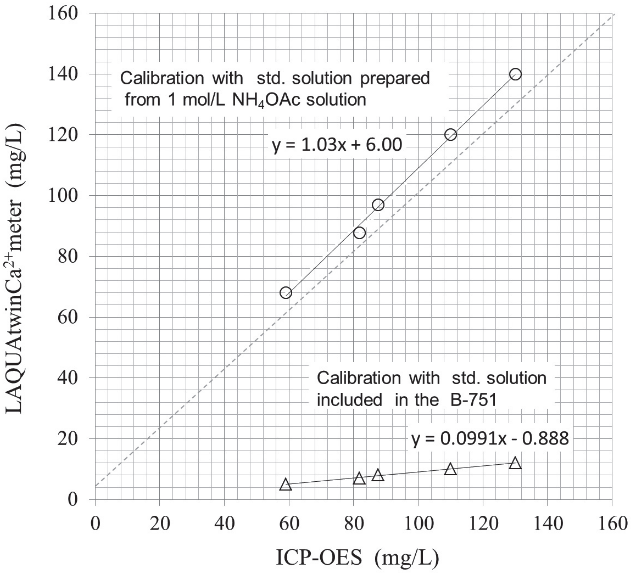

Figure 3 Plots of LAQUAtwinCa^{2+}meter vs. ICP-OES for extracted calcium ion concentration in 1 mol/L ammonium acetate (NH_4OAc) solution. LAQUAtwinCa^{2+}meter calibrated with Ca^{2+} std. solutions prepared by the addition of 1 mol/L NH_4OAc solution (○) and Ca^{2+} std. solutions containing 0.1 mol/L KCl as accessories included in the B-751 (△).

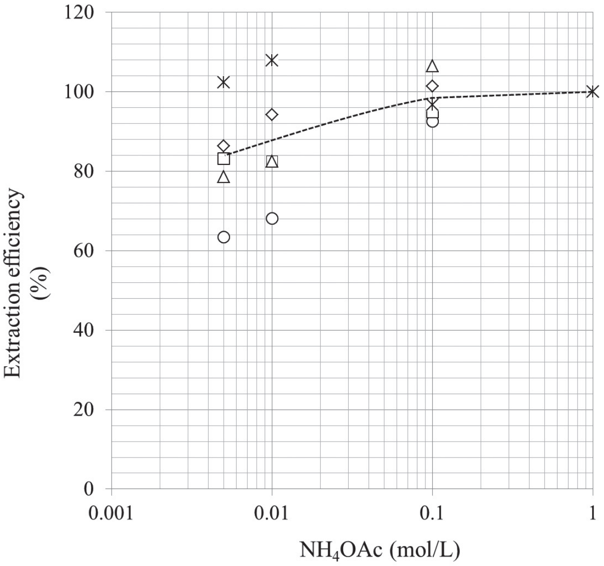

Figure 4 Variation of extraction efficiency with ammonium acetate (NH_4OAc) concentration. Soil samples: Green pepper (○), tomato (△), spinach (□), lettuce (◇) and kale (✻). Dotted line indicates the trend of average value of 5 items each NH_4OAc concentration.

Table 1 shows the results of measurement of calcium ion concentration in 1 mol/L NH_4OAc solution by ICP-OES and LAQUAtwinCa^{2+} meter. When LAQUAtwinCa^{2+} meter was calibrated by calcium ion standard solutions containing 0.1 mol/L potassium chloride as supporting electrolyte, which were included in LAQUAtwinCa^{2+} meter accessories, the results obtained by LAQUAtwinCa^{2+} meter were about 10 times lower than those of ICP-OES. On the other hand, by calibration with calcium ion standard solutions containing 1 mol/L NH_4OAc solution as the same concentration in soil extraction solution, the results obtained by LAQUAtwinCa^{2+} meter agreed with the same order of those of ICP-OES. And results of LAQUAtwinCa^{2+} meter were plotted against those of ICP-OES as shown in Figure 3. In regard to 1 mol/L NH_4OAc solution, the slope meaning the relationship between two methods was approximately 1, and also the correlation coefficient was R = 0.998 (n = 5).

Measurements of exchangeable potassium ion with LAQUAtwinK$^+$ meter

In the measurement of potassium ion concentration by using ISE method, it is difficult to measure potassium ion concentration accurately in the presence of large amount of NH_4OAc because the K$^+$ selective sensor is subject to interference from ammonium ion. This interference means that the electric potential difference are generated in response to other undesired ions. The extent of interference from other ions vary according to the varieties of objective ion and interfering ions and the proportion of these coexistence ions. Table 2 shows the results of potassium ion concentration in 1 mol/L and 0.01 mol/L NH_4OAc extraction solution measured by using ICP-OES and LAQUAtwinK$^+$ meter. Furthermore, Figure 4 shows the variation of extraction efficiency with

Table 1 Results of calcium ion concentration extracted by 1 mol/L ammonium acetate (NH_4OAc) solution.

Grove soil	Calcium ion concentration (mg/L)			CaO (mg/100 $g_{\text{air-dried soil}}$)	
	ICP-OES	LAQUAtwinCa^{2+}meter		ICP-OES	LAQUAtwinCa^{2+}meter
		Calibration with std. sol. prepared from 1 mol/L NH_4OAc solution	Calibration with std. sol. included in B-751※		Calibration with std. sol. prepared from 1 mol/L NH_4OAc solution
Green pepper	130	140	12	360	390
Tomato	110	120	10	310	340
Spinach	82	88	7	230	240
Lettuce	88	97	8	240	270
Kale	59	68	5	160	190

※Ca^{2+} std. solutions containing 0.1 mol/L KCl.

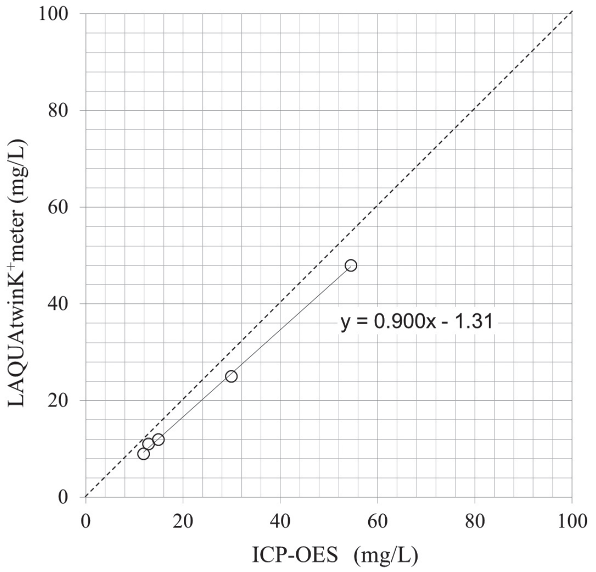

Figure 5 Plots of LAQUAtwinK$^+$meter vs. ICP-OES for extracted potassium concentration in 0.01 mol/L ammonium acetate (NH_4OAc) solution.

NH_4OAc concentration, regarding the potassium ion concentration of 1 mol/L NH_4OAc solution measured by ICP-OES as 100% extraction efficiency.

As shown **Table 2**, for 1 mol/L NH_4OAc extraction solution, the values of LAQUAtwinK$^+$ meter were higher than those of ICP-OES because LAQUAtwinK$^+$ meter is influenced by ammonium ion as interfering ion. On the other hand, for 0.01 mol/L NH_4OAc solution, the values of LAQUAtwinK$^+$ meter were generally consistent with those of ICP-OES, though the extraction efficiency was down about 80% by using 0.01 mol/L NH_4OAc solution (see **Figure 4**). In **Figure 5**, for 0.01 mol/L NH_4OAc solution, the plots of the results of LAQUAtwinK$^+$ meter against those of ICP-OES were strongly correlated (correlation coefficient R = 0.999). So the measurement of potassium ion by LAQUAtwinK$^+$ meter is possible by using the extraction method by 0.01 mol/L NH_4OAc solution which provide not too low extraction efficiency and resulted in high correlation with the result of ICP-OES. However, in this way, the result obtained by LAQUAtwinK$^+$ meter must be converted to extraction from 1 mol/L NH_4OAc solution. Also, the effect of the decrease of concentration of NH_4OAc solution to extraction efficiency varied depending on potassium ion concentration in soil extraction solution, so this measurement method should be available to roughly estimate the value of potassium ion concentration.

Application to the Result of Soil Test

When the results obtained by LAQUAtwin ion meter is applied to the result of soil test, the calcium ion and potassium ion concentrations obtained by LAQUAtwinCa^{2+} meter and LAQUAtwinK$^+$ meter should be indicated as mass (mg) of calcium oxide (CaO) and potassium oxide (K_2O) per 100 g dried soil, respectively. The conversion formulas were indicated as describe below[1].

The conversion formula used for converting calcium ion (Ca^{2+}) concentration into $CaO_{(mg/100\text{ g dried soil})}$

$$CaO_{(mg/100\text{ g dried soil})} = [Ca^{2+}{}_{(mg/L)}] \times \left(\frac{a}{1000}\right) \times \left(\frac{100}{b}\right) \times 1.399 \quad \cdots\cdots (1)$$

The conversion formula used for converting potassium ion (K^+) concentration into $K_2O_{(mg/100\text{ g dried soil})}$

$$K_2O_{(mg/100\text{ g dried soil})} = [K^+{}_{(mg/L)}] \times \left(\frac{a}{1000}\right) \times \left(\frac{100}{b}\right) \times 1.205 \quad \cdots\cdots (2)$$

a: The volume of NH_4OAc solution for extraction (mL)
b: The mass of soil sample for extraction (g)

Table 2 Results of potassium ion concentration extracted by 1 and 0.01 mol/L ammonium acetate (NH_4OAc) solution.

Grove soil	Potassium ion concentration (mg/L)				K_2O (mg/100 $g_{\text{air-dried soil}}$)	
	Extraction by 1 mol/L NH_4OAc solution		Extraction by 0.01 mol/L NH_4OAc solution		ICP-OES	LAQUAtwinK$^+$ meter
	ICP-OES	LAQUAtwinK$^+$ meter	ICP-OES	LAQUAtwinK^{+}※ meter		
Green pepper	80	170	55	48 (71)	190	170
Tomato	36	140	30	25 (30)	87	73
Spinach	16	130	13	11 (13)	38	32
Lettuce	16	130	15	12 (13)	38	31
Kale	11	120	12	9 (8)	26	20

※The values within ( ) indicate the results obtained from 0.01 mol/L NH_4OAc solution converted into 1 mol/L NH_4OAc solution values using each extraction efficiency. Each extraction efficiency at 0.01 mol/L NH_4OAc solution for the following vegetable soils are green pepper 68%, tomato 82%, spinach 82%, lettuce 94% and kale 107%. The values of K_2O for LAQUAtwinK$^+$meter were calculated from converted potassium ion concentration.

As reference, calculated values $CaO_{(mg/100 \text{ g dried soil})}$ and $K_2O_{(mg/100 \text{ g dried soil})}$ from the measured ion concentrations in this report were listed in Table 1 and Table 2, respectively.

Conclusion

In this report, simplified analysis methods are introduced which exchangeable calcium ion and exchangeable potassium ion in soil samples were measured by using LAQUAtwin. LAQUAtwin series are compact and portable simplified meters as independent of the situation to measure. However, to obtain the correlation to other large instruments, the measurement procedure considered the effect of interfering ion and the dissociation of objective ion should be needed. I would like to develop and suggest the measurement procedure applicable to various fields in the future.

References

[1] http://www.maff.go.jp/j/seisan/kankyo/hozen_type/h_sehi_kizyun/ibaraki01.html, (2013.06.25 17:00).

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