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Preparation of Quality Control Material for Assuring Quality of Electrical Conductivity Measurements in Soil

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ACCURATE and reliable analytical results of soil have become essential tool for understanding salinity and limiting factors affecting agricultural productivity. Reliability of results depends mainly on the existence and quality of reference materials which are considered as crucial tools for validation and verification of the analytical process and assuring quality of measurement results. The National Metrology Institute of Egypt [NIS] is striving to set up the national standards to ensure all measurement results are traceable to the international system of unit (SI). NIS starting development of a series of soil reference materials to meet Egyptian requirements and customer demands. This article describes the production process of the soil reference material characterized for electrical conductivity from processing to value assignment. Characterization, homogeneity and stability studies of the material were carried out according to ISO guides 34, 35 and 80. The measurement results were statistically analyzed to calculate assigned values. The assigned value and expanded uncertainty for $EC_{1:1}$ and $EC_{1:5}$ methods were found 1234 ±58 µS/cm and 973 ±52 µS/cm, respectively.

Keywords: Electrical Conductivity, Soil, Quality Assurance, Secondary reference material.

Introduction

Electrical conductivity (EC) of a soil extract is the most widely used parameter for describing soil salinity and concentration of dissolved mineral salts present in the soil [1]. Electrical conductivity estimates the concentration of ions in the soil, and consists predominately of the cations Na^+, Ca^{+2},K^+, and Mg^{+2} and the anions Cl^-, $SO4^{-2}$ and HCO_3^-[2,3]. Salinity is one of the most severe environmental factors limiting the productivity of agricultural crops. Until the 1950's, the salt contents of soils were estimated from the electrical conductivity of saturated soil pastes. As a result of progress made in the understanding of saline soils, it was found that the plant responds to the salt concentration of soil solution rather than the total salt content of the soil. Therefore, the conductivity of the saturation extract is recommended as a general method for estimating soil salinity in relation to plant growth [1, 4]. Extract based on soil to water ratios of 1:1, 1:2,1:2.5, 1:5, and 1:10 are commonly used to determine the EC values of soils but ratios of 1:1 and 1:5 are mainly used by routine and ISO/IEC 17025 accredited testing laboratories applying standard methods for consistent determination of EC of a soil [1, 5-6]. The result of EC depends on shaking, stirring, agitation, equilibration times, centrifuging, or filtration procedures that have been used to prepare extracts. The aim of this research work was to prepare a reference material from soil characterized for EC to be used in analytical method validation, variations control in the preparation of extract, and verification of the accuracy of measurements. The preparation process described in this paper includes steps of material processing, homogeneity testing, stability study, characterization and value assignment [7, 8].

Materials and Methods

Chemicals and reagents

Potassium chloride standard solution, 1408 µS/cm prepared according to OIML R56 and IUPAC technical reports[9, 10]. The solution used for quality control procedures and establishing traceability of measurement results. High purity water was obtained through a Milli-Q water purification system used. (Millipore, Bedford, MA, USA) and was used in all procedures.

Equipment

Conductivity meter with automatic temperature

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correction (Thermo electron corporation, ORION 4STAR, USA), five digit analytical balance (Sartorius, Germany), shaking machine (Barnstead, USA), waterbath for temperature control(DAIHAN Scientific, KOREA), Whatman filter paper and class A glassware.

Materials Processing and Packaging

Soil samples were obtained from Al-Fayoum governorate (Al-Fayoum, Egypt).30 kilograms were mixed by shaking and packed in 500 mL high density polyethylene bottles to prevent humidity uptake, the bottles were stored at room temperature in the dark.

Extraction procedures

1:5 Ratio [$EC_{1:5}$]: Ten grams of air-dry soil sample were accurately weighed and transferred to shaking bottle. 100 mL of ultra-pure water were added at a temperature of 20 ±1 °C. The bottle was closed and placed in a horizontal position in the shaking machine. The samples were shaken for 30 min. then filter directly through a filter paper [1, 6]. The electrical conductivity of the filtrates was measured by the conductivity meter at a temperature of 25 ±0.1 °C.

1:1 Ratio [$EC_{1:1}$]: 50 grams of air-dry soil sample were accurately weighed and transferred to glass beaker. 50 mL of ultra-pure water were added at a temperature of 20 ±1 °C. The suspensions are mixed well with a glass rod, and allowed to stand for 30 minutes. The suspensions were stirred every 10 minutes during this period and after one hour [1, 5]. Then filtered directly through Whatman filter paper. The electrical conductivity of the filtrates was measured by the conductivity meter at a temperature of 25 ±0.1 °C.

Homogeneity study

The homogeneity study was designed to quantify any between bottle heterogeneity of the electrical conductivity values. A total of 10% of the bottles were selected using random stratified sampling of the whole batch. Five subsamples per bottle were analyzed three times for each sample. All samples were analyzed under repeatability conditions. One way-Analysis of Variance (ANOVA) was used to check the homogeneity of the samples.

Stability study

Ten bottles were selected randomly for stability study, the bottles were stored at room temperature for 0, 2, 4, 6 and12 months.Three samples were analyzed in replicates at each time point. The data were checked for outliers and a linear regression analysis as a function of time was performed. Slopes were tested for significance using a t test [8].

Results and Discussion

Results of homogeneity study

The results of the homogeneity study were analyzed [Fig.1] and uncertainty of the material was estimated and combined with other sources to estimate expanded uncertainty [11-13].

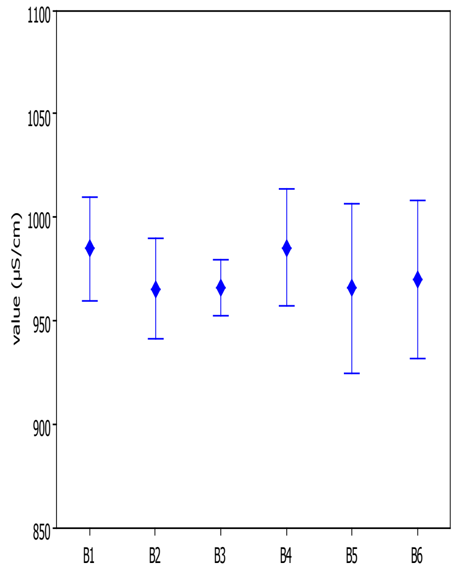

Fig.1. Results of between-bottle homogeneity study of electrical conductivity in soil expressed as µS/cm.

The uncertainty u_{bb} was estimated from the difference between the total variability and the within bottle variability [8, 14-19] using equation 1 and 2.

$$\sigma_h(u_{bb}) = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (1)$$

$$\sigma_h(u_{bb}) = \sqrt{MS_{within}/n}\cdot\sqrt[4]{2/(\nu MS_{within})} \quad (2)$$

In case of $MS_{between}$ is larger than MS_{within}, both equations were applied and the largest uncertainty value was selected. The largest uncertainty values were obtained from Eq. (2) because $MS_{between}$ are smaller than MS_{within} for both methods, which indicates poor repeatability of the measurement method and this is acceptable in measurement of electrical conductivity in soil.

Characterization

As described in the ISO Guide 35 [8], the property values of reference materials shall be determined by measurement using a single primary method, measurement with two or more independent reference methods, or two additional approaches that involve a network of laboratories, using one or more methods of demonstrable accuracy or also a method-specific approach giving only method-specific assessed property values.

The characterization of the material was conducted using method-specific approach to estimate method-specific values of electrical conductivity. The characterization of the material was based on soil to water ratios, shaking, stirring, agitation, equilibration times and filtration of extracts. The experimental set-up of the characterization study was designed to evaluate EC values and associated variability. For quantitative determination of EC values of the soil material, six bottles were selected from the whole set of 60 bottles and five independent subsamples were measured in five different days using $EC_{1:1}$ and $EC_{1:5}$ methods. Traceability of the measurements results was established by calibrating conductivity meter with potassium chloride standard solution, 1408 µS/cm prepared according to OIML R56 and IUPAC guidelines [9, 10] at 20 ^{o}C before analysis. The measurement results of each method (Table 1) were statistically analyzed to test normality and precision. Good reproducibility of data obtained from each method indicate that the study could be continued to produce a fully certified soil reference material.

TABLE 1. Results of characterization study of electrical conductivity in soil for $EC_{1:1}$ and $EC_{1:5}$ methods expressed as µS/cm.

Method	Bottle	Day 1	Day 2	Day 3	Day 4	Day 5
$EC_{1:1}$	B_1	1211	1234	1192	1275	1261
	B_2	1200	1241	1230	1260	1231
	B_3	1240	1252	1215	1235	1216
	B_4	1255	1263	1190	1248	1270
	B_5	1272	1228	1244	1231	1190
	B_6	1261	1229	1220	1247	1190
	Average	**1240**	**1241**	**1215**	**1249**	**1226**
	S	**29**	**14**	**21**	**16**	**34**
$EC_{1:5}$	B_1	1014	953	972	978	982
	B_2	970	942	948	995	943
	B_3	993	967	969	1018	927
	B_4	963	993	965	957	1011
	B_5	986	974	976	980	967
	B_6	938	967	1008	995	944
	Average	**977**	**966**	**973**	**987**	**962**
	S	**26**	**18**	**20**	**21**	**31**

Results of stability study and assigning material shelf life

Data was plotted as a function of time and the regression line was checked by using a t-test for significant trends possibly indicating change in electrical conductivity values of the material [Fig.2]. The short- and long-term stability results were evaluated regarding absence of outliers in residual plots.

For the short-term stability studies, the results were used to state the maximum time periods allowed for transportation of the material. For the long-term stability studies, the values of uncertainties were calculated as uncertainty of the slope of the regression line [8, 11-13, 20] and incorporated in expanded uncertainty of the material. The prediction of the material shelf life was based on standard uncertainty due to long term stability [8] and uncertainty allowance due to instability was evaluated according to the Eq. 3.

$$u_{lts} = Y_0 X u_b \quad (3)$$

Where, Y_0 is initial value, X is time point and u_b is standard uncertainty due to long term stability

After certification, the reference materials keep on being monitored under storage conditions to maintain confidence in the status of the prepared reference materials.

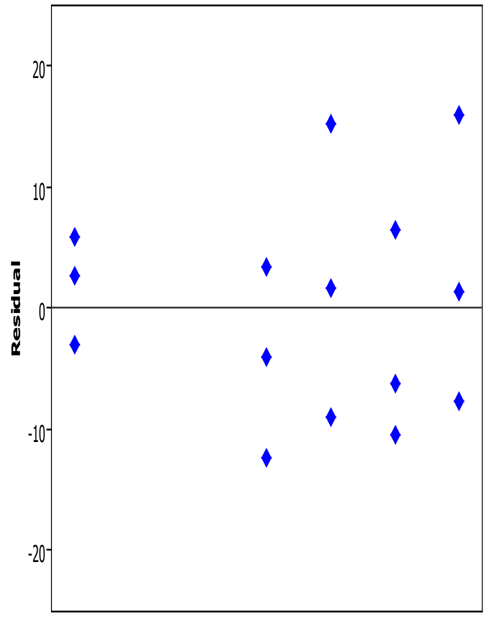

Fig.2. Results of stability study of electrical conductivity in soil expressed as µS/cm.

Value assignment

The certification of the material was performed according to ISO Guides 34:2009 [7] and 35:2006 [8]. The assigned value was calculated as the robust mean from characterization results of each method [7, 21-22]. Kernel density plots were additionally used to identify modes in the measurement results and to confirm assigned value [Fig.3]. Expanded uncertainty is derived from the uncertainty components due to sample inhomogeneity (u_{bb}), short term and long term stability (u_{sts}, u_{lts}) and characterization (u_{char}). The uncertainties contributed to characterization include precision ($u_{precision}$) of the analysis (repeatability and reproducibility), uncertainty of standard solution used (u_{CRM}) and mass of the samples (u_{sample}). Expanded uncertainty is expressed as two times the root of the sum of the squares of u_{bb}, u_{sts}, u_{lts}, and u_{char} at a confidence level of approximately 95 % [23-25], the certified values for $EC_{1:1}$ and $EC_{1:5}$ methods are 1234 ±58µS/cm and 973 ±52 µS/cm, respectively.

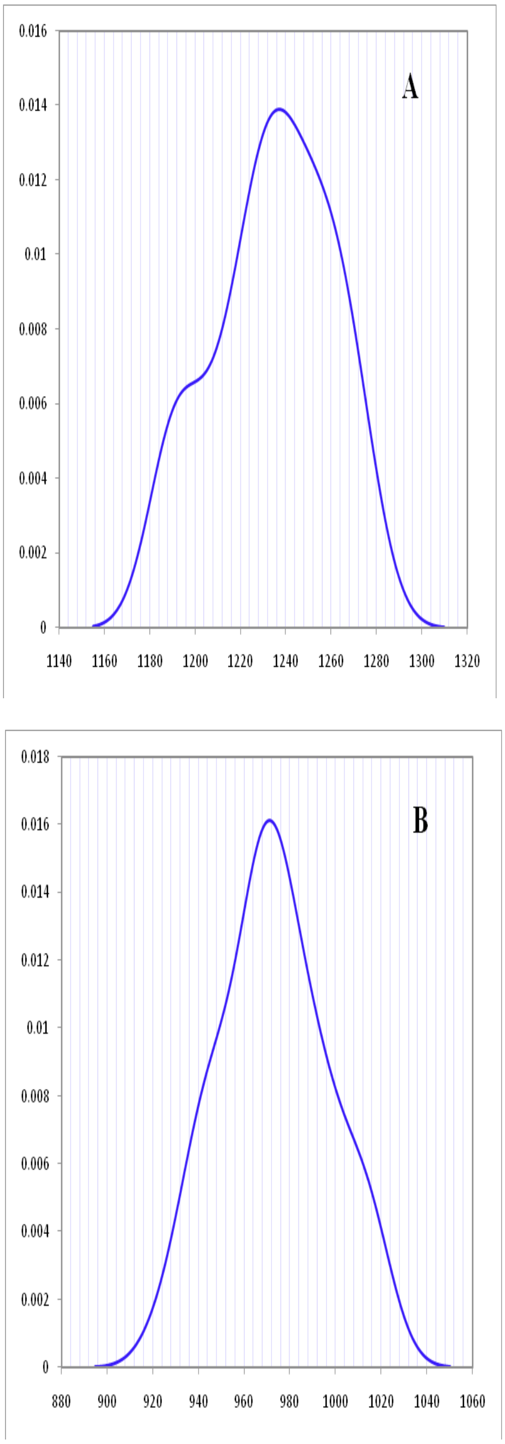

Fig. 3. Kernel density plots for measurement results of EC1:1 (A) and EC1:5 (B) methods

Conclusion

The certification of electrical conductivity in soil by National Institute of Standards was appropriately concluded. The development of such materials intends to fulfill the strong demand for soil reference materials, due to lack of availability of such materials in the market, the material will be a useful tool for the assurance quality of measurement results, validation of analytical methods and establishing traceability of measurement results to the International System of Units (SI), in order to ensure their accuracy, reliability, and comparability over space and time. Certification was carried out in full compliance with ISO Guides 30-35 and measurement results were statistically treated and the certified values for $EC_{1:1}$ and $EC_{1:5}$ methods are 1234 ±58 µS/cm and 973 ±52 µS/cm, respectively.

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تحضير مادة مرجعية لتوكيد جودة نتائج قياسات التوصيلية الكهربية في التربة

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تعتمد جودة نتائج قياس التوصيلية الكهربية للتربة علي القياس بإستخدام طرق تقدير مناسبة مدعومة بطرق تأكيد للجودة. وتعتبر المواد المرجعية افضل وسيلة لتوكيد الجودة وتحديد الاخطاء في القياس ومعايرة الطرق واقرار صلاحيتها وحيث ان التوصيلية الكهربية هي احد القياسات المهمة وذلك لإستخدامها في الحكم علي حموضة وقلوية التربة فقد تم تطوير مادة مرجعية للتأكد من صحة النتائج وتوكيد جودتها وتم تحضير المادة المذكورة طبقا للطرق القياسية الدولية وتم معالجة النتائج إحصائيا لحساب القيم الموصفة واللايقين المصاحب عند مستوي ثقة محدد.