ESTIMATION OF MEASUREMENT UNCERTAINTY FOR POTASSIUM IN ORGANO-MINERAL FERTILIZERS

Traian Mihai CIOROIANU, Carmen SÎRBU, Daniela MIHALACHE

National Research and Development Institute for Soil Science, Agro-chemistry and Environment
Protection - RISSA Bucharest, 61 Marasti Blvd, 011464, District 1, Bucharest, Romania

Corresponding author email: carmene.sirbu@yahoo.ro

Abstract

Along with nitrogen and phosphorus, potassium is one of the primary nutrients that provides significant yield increases when applied in amounts necessary for crop development. In order to avoid environmental pollution and to ensure the necessary content of this nutrient, it is important to know the amount of soluble potassium in the applied fertilizers. This article presents the evaluation of some parameters for estimation of measurement uncertainty for water-soluble potassium in organo-mineral fertilizers. Potassium was determined by flame-photometric method and the expanded uncertainty (U) of the method, obtained by multiplying the combined uncertainty by the coverage factor $k = 2$ (confidence level 95%) was 10.18%. The determinations were performed on a sample of organo-mineral fertilizer with a complex matrix and known composition in which the average of the determinations was 12.69% K_2O.

Key words: measurement uncertainty, potassium, organo-mineral ferilizers, flame photometric method.

INTRODUCTION

Knowing the composition of fertilizers is a priority for all users. Manufacturers are obliged to declare the composition and to comply with the tolerances imposed by the legislation in force. Currently, in Romania, both national (Order no. 6/2004) and European legislation (Regulation (EC) no. 2003/2003) on fertilizers provide for tolerances on nutrient composition. Currently, in Regulation (EC) no. 2003/2003 for the analysis of the fertilizers provided in Annex I List of types of EC fertilisers, for determination of potassium is provided in the standard EN 15477: Fertilisers - Determination of the water-soluble potassium content. According to this Annex, given the sources of raw materials and the types of fertilizers provided, producers need only declare the water-soluble potassium content.

Agriculture is one of the sectors that contributes greatly to the world's greenhouse gas emissions. The use of raw materials obtained from the recycling of by-products from agricultural and industrial activities allows the return to the production chain, which can be beneficial both economically and ecologically and it is part of the concept of circular economy (Crusciol et al., 2020; Liu et al., 2020). Currently, on the market are sold fertilizers from the category "organic", "organo-mineral" with variable content of organic substances from various sources. In this context, the variety of raw materials makes it difficult to find a method for determining the composition of fertilizers. As the water-soluble potassium content is an indication of the immediate availability of this nutrient for plant nutrition, its determination is of great importance to farmers. In addition to this, we must keep in mind that potassium applied in improper amounts can lead to environmental pollution or poor nutrition.

All measurements are affected by errors and the measurement uncertainty tells us the size of the measurement error (Magnusson et al., 2017).

As defined in Regulation (EC) no. 2003/2003, a solid organo-mineral fertilizer shall contain at least one of the following declared primary nutrients: nitrogen (N), phosphorus pentoxide (P_2O_5) or potassium oxide (K_2O) and the content of total potassium (K_2O) should be at least 2%. The determinations presented in this paper were made on a matrix of organo-mineral fertilizer with a content of 12% K_2O.

Potassium plays an important role in plant development (Çalişkan & Çalişkan, 2019). Potassium is an essential nutrient for plant

growth (Marschner, 1995; Nieves-Cordones et al., 2019). Potassium helps in alleviating detrimental effects of salt stress (Kumari et al., 2021) influencing the chlorophyll content (Kaya et al., 2001).

A useful measure used to demonstrate the quality of results is measurement uncertainty (Ellison & Williams, 2012), and laboratories need this parameter to verify their own measurement quality, given that estimating measurement uncertainty is a requirement in SR EN ISO 17025: 2018. All measurements are affected by errors and the measurement uncertainty provides information about the size of the measurement error. Therefore, measurement uncertainty is an important part of the reported result (Magnusson et al., 2017).

Ignoring the value of the uncertainty of the composition of a fertilizer can lead to an overestimation of its efficiency (Khor & Zeller, 2014).

The use of validated methods is important for an analytical laboratory to show its qualification and competency. Method validation is done by evaluating a series of method-performance characteristics, such as precision, trueness, selectivity/specificity, linearity, operating range, recovery, limit of detection (LOD), limit of quantification (LOQ), sensitivity, robustness, measurement uncertainty (Magnusson & Örnemark, 2014).

This paper focuses on estimating the measurement uncertainty related to water-soluble potassium determination by the flame photometric method in organo-mineral fertilizers.

MATERIALS AND METHODS

Reagents and solutions

An organo-mineral fertilizer reference material with the following characteristics was used:
- assigned value: m = 12.69% K_2O and uncertainty, u = ± 0.19%;
- standard deviation of the mean: s = 0.88%;
- tolerance range: 11.89-13.49%.

The sample was finely ground in order to obtain a representative sample for analysis.

For the preparation of the working standard solutions of organo-mineral fertilizer samples, a standard potassium solution of 1000 mg/L traceable to the NIST was used. Potassium standard solution and H_2SO_4 95-97% (used to prepare 1N solution) of analytical grade were obtained from Merck (Germany). All solutions were prepared using distilled water (purity class 2), according to the standard SR EN ISO 3696.

Equipments

All weighing operations were carried out using METTLER TOLEDO AG204 analytical balance. Potassium content was determined with the Flame Photometer model Sherwood 410 with a preloaded filter stick for K.

Preparation of Working Standard Solutions

Working standard solutions containing 0.00, 2.00, 4.00, 6.00, 8.00, 10.00 K μg/mL were prepared by proper dilutions of the 1000 mg/L potassium standard. For every 100 mL of prepared standards, 10 mL of 1N sulfuric acid was added. The volumetric flask was filled to the mark with distilled water.

Method description

Flame photometry is part of atomic emission spectrometry and aims to determine the qualitative and quantitative elements based on the interpretation of emission spectra. The potassium in the sample is dissolved in boiling water. After elimination or fixation of substances that may interfere with the quantitative determination, potassium is determined based on the interpretation of the emission spectra using a flame photometer. The temperature of the flame ensures the melting and evaporation of the salt, the dissociation of the molecules and the excitation of the atoms formed.

During the determinations, the temperature was monitored using a thermo-hygrometer (t = 20 ± 4ºC).

Spray each standard solution successively into the flame of the flame photometer and note the intensity of the radiation emitted. After each standard solution, water is sprayed into the flame. For each standard solution 3 sprays are made, and as a result the average of the three indications of the emitted radiation intensity is considered.

It is known that the number of replicates of the calibration standards is an excellent way to minimize the random calibration error and then

to increase the accuracy of the values in the measurements of the samples (Raposo, 2016).

In order to evaluate the parameters of the calibration line, the calibration curve is drawn, considering on the ordinate the intensity of the emitted radiation, and on the abscissa the corresponding potassium content (µg/mL).

Calibration curve

From the practical experience of the laboratory and the evaluations performed (ISO 8466-1: 1990), the linearity range in the determination of potassium is $0.5 \div 10$ µg/mL which is in accordance with the equipment manufacturer's instructions ($0.5 \div 20$ µg/mL) (Sherwood-model-410).

RESULTS AND DISCUSSIONS

The measurement uncertainty was calculated by following an internal procedure and international guidelines (Ellison & Williams, 2012). The evaluation of measurement uncertainty of water-soluble potassium determination consisted in: specification of the measurand, identification of uncertainty sources, quantification of uncertainty components and calculation of combined and expanded uncertainty.

Specification of the measurand

The potassium content of the organo-mineral fertilizer, expressed as a percentage of potassium oxide (K_2O), shall be calculated according to the following formula:

$$\% \ Potassium\left(K_2O\right) = \frac{c \cdot v \cdot d_1 \cdot d_2 \cdot 100}{m \cdot 10^6} \times 1.2 \quad (1)$$

where:
v - the volume of extract from the sample, (mL);
m - mass of the sample, (g).
c - the concentration of potassium corresponding to the intensity of the emitted light read on the calibration curve (µg/mL);
1.2 - conversion factor for potassium (K) in potassium oxide (K_2O);
d_1 - coefficient of the first dilution (ratio between the volume of the intermediary dilution and aliquot 1);
d_2 - coefficient of the second dilution (ratio between the volume of the final dilution and aliquot 2).

Identification of uncertainty sources

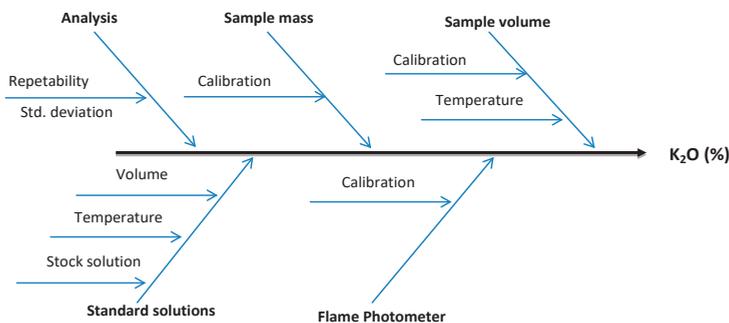Figure 1 illustrates the cause-and-effect diagram for the standard uncertainty of the method.

Figure 1. Cause and effect diagram for water-soluble potassium determination by flamephotometric method

As schematized in Figure 1, the following sources of were identified: (a) uncertainty from the standard and standard dilution to obtain the working calibration solutions; (b) uncertainty from the flame-photometer; (c) the dilution factor includes the contributions of uncertainties from the volumetric flasks and pipettes and the volume expansion at the laboratory temperature; (d) uncertainty related to the sample mass/analytical balance (calibration certificate); (e) repeatability, evaluated by measuring 10 sample replicates. The measurements were conducted by the same analyst using the same flame-photometer instrument under the same working conditions.

Quantification of individual components
Repeatability
All steps of the measurement procedure (Figure 1) were included in the uncertainty associated with the repeatability of the overall experiment. Repeatability data is given in Table 1.

Table 1. Repeatability of the flam-photometric method for determination of potassium in organo-mineral fertilizer (OMF) (secondary reference material)

Sample	% water-soluble potassium (% K_2O)
Replicate 1	12.686
Replicate 2	12.687
Replicate 3	12.920
Replicate 4	12.687
Replicate 5	12.450
Replicate 6	12.215
Replicate 7	12.686
Replicate 8	13.156
Replicate 9	13.390
Replicate 10	11.981
Statistical parameters	% K_2O
Average value	12.686
Standard deviation, n = 10	0.414

Sample mass, dilution factor and flame-photometer contribution
The uncertainty related to the calibration of all equipment was evaluated using the data from the calibration certificates. The standard uncertainty associated with the mass of the sample was calculated (Eq. 2), using the data from the calibration certificate (De Oliveira, 2016). This contribution was counted twice, once for the tare and once for the sample weight, because each is an independent observation and the linearity effects are not correlated (Ellison & Williams, 2012). Standard uncertainties u(x) were calculated according to the following equations:

$$u(m) = \sqrt{\left(\frac{U_{eccentricity}}{2}\right)^2 + \left(\frac{U_{linearity}}{2}\right)^2} \qquad (2)$$

$$u(v) = \sqrt{\left(\frac{U_{calibration}}{2}\right)^2 + \left(\frac{V_{temp}}{\sqrt{3}}\right)^2} \qquad (3)$$

$$u(x) = \frac{U_{calibration}}{2} \qquad (4)$$

For all volumetric equipment the uncertainty consists of 2 components: calibration uncertainty and uncertainty due to the volume expansion at laboratory temperature (20±4ºC), calculated by means of Eq. 5 (Ellison & Williams, 2012):

$$V_{temp} = V_{calibration} \times Dt \times 2.1 \times 10^{-4} \qquad (5)$$

where:
V_{temp} - uncertainty due to the volume expansion at laboratory temperature;
$V_{calibration}$ - volumetric glassware uncertainty according to calibration certificate;
2.1×10^{-4} °C^{-1} - coefficient of volume expansion for water;
Dt - temperature variation in the laboratory (20±4ºC).

Standard uncertainty due to sample dilution was estimated by summing the uncertainties of the volumetric glassware to the volume expansion (Table 2). The relative uncertainties due the dilution factor of the sample (volumetric flasks and pipettes) were combined into one contribution. Standard uncertainty related to the flame-photometer equipment was calculated by means of Eq. (4).

Working standard solutions and stock solution contribution
An example for the preparation of one working standard solution is summarized in Table 3. The same procedure was repeated for all standards. Standard uncertainty associated to the stock solution was estimated by means of Eq. 4 (Table 3). The relative uncertainty related to the dilution of the standards was obtained by the sum of the relative uncertainties due to the dilution factor and stock solution.

The relative contribution of each component, as well as the combined and combined standard uncertainties are summarized in Table 4. The combined standard uncertainty of the method was estimated according to Eq. (6). The expanded uncertainty of the method (U) was obtained by multiplying the combined uncertainty with a coverage factor of 2.

$$u(K_2O) = \bar{x}\sqrt{u(r)^2 + u(m)^2 + u(l)^2 + u(c)^2 + u(v)^2 + u(e)^2} \quad (6)$$

To calculate combined uncertainty for potassium determination in organo-mineral fertilizer by flame-photometer method, Eq. (7) was used, and the value 5.09% was obtained.

$$U_c = (u_c \times 100) / \bar{x} \qquad (7)$$

The extended uncertainty (U) of the method is calculated by multiplying the standard uncertainty combined with a coverage factor k = 2, which gives a level of confidence of approximately 95% (Eq. 8) and a value of 10.18% was obtained.

$$U = U_c \times 2 \qquad (8)$$

The result of water-soluble potassium in organo-mineral fertilizers of measurement and the expanded uncertainty estimated by using Eurachem guidelines (Ellison & Williams, 2012) was 12.686 ± 1.29 % K_2O.

Bias of the method is expressed as analytical recovery (value observed divided by value expected) and the value of 0.3% was obtained.

Table 2. Standard uncertainties related to sample mass, dilution factor and flame-photometer

Source/ Quantity	Uncertainty components		Distribution		Eq. (no)
Analytical balance					
Mass of the sample 2.5 g	Eccentricity 0.0005 g/	Linearity 0.0002 g	normal 2	normal 2	Eq. (2)
Dilution factor (volume)					
Volumetric flask (v1) 500 mL	Calibration 0.05 mL	Volume expansion 0.2425 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Volumetric flask (v2) 250 mL	Calibration 0.03 mL	Volume expansion 0.121 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Volumetric flask (v2) 100 mL	Calibration 0.03 mL	Volume expansion 0.0485 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Aliquot 1 25 mL	Calibration 0.02 mL	Volume expansion 0.0121 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Aliquot 2 10 mL	Calibration 0.023 mL	Volume expansion 0.0048 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Flame photometer	Calibration 0.570 µg / mL		normal 2		Eq. (4)

Table 3. Standard uncertainties related to the preparation of working standard solutions and to the stock standard solution

Source/ Quantity	Uncertainty components		Distribution		Eq. (no)
Dilution factor (volume)[i]					
Burette 2 mL	Calibration 0.015 mL	Volume expansion 0.00097 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Volumetric flask 100 mL	Calibration 0.03 mL	Volume expansion 0.0485 mL	normal 2	rectangular $\sqrt{3}$	Eq. (3)
Stock solution[ii]					
Concentration 1000 mg/kg	Calibration 5 mg/kg		normal 2		Eq. (4)

[i]Standard uncertainty related to the preparation of one working standard solution
[ii]Standard uncertainty related to the stock standard solution

Table 4. The relative contribution of the uncertainty components and combined standard uncertainties for potassium determination in organo-mineral fertilizer by flame-photometer method

Uncertainty component	Value	Type
Potassium content mean, %	12.686	A
Relative uncertainties of the repeatability, u(r)	0.0327	A
Relative uncertainties of the calibration solutions, u(c)	0.0052	A & B
Relative uncertainties of the linearity range, u(l)	0.0151	A
Relative uncertainties of the balance, u(m)	0.00008	B
Relative uncertainties of the flask / pipette, u(v)	0.0014	B
Relative uncertainties of the flam photometer, u(e)	0.0356	B
Combined standard uncertainty (u_c)	0.6458	A+B
Combined uncertainty $(U_c = (u_c \times 100) / \bar{x}$ of the method	5.09	%
Expanded uncertainty, $k=2$ $(U = U_c \times 2)$ of the method	10.18	%

Uncertainty budget

The uncertainty budget as relative contributions of the different components are shown in Figure 2.

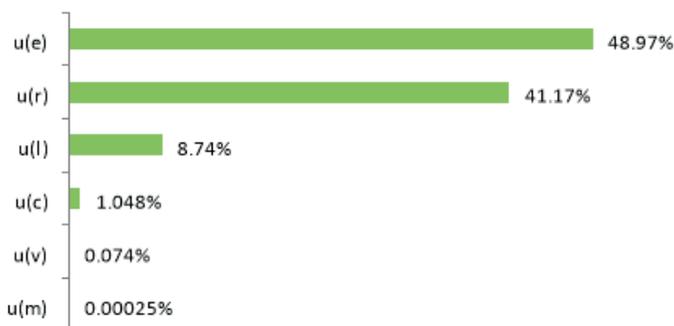As shown in Figure 2, the main sources of uncertainty of the result of measurement were contributions from repeatability, standard solutions preparation and flame-photometer instrument, whereas the contribution of the balance (sample mass) and volumetric glassware had no influence on the overall uncertainty budget.

Figure 2. The uncertainty contributions as relative uncertainties (as coded in Table 4)

CONCLUSIONS

This study evaluated the measurement uncertainty of the result of water-soluble potassium determination by flame-photometer instrument in organo-mineral fertilizers.

The identified uncertainty components were the repeatability, standard solution dilutions, flame-photometer, linearity range, sample mass (anaytical balance) and sample dilution factor. It was observed that the largest contribution comes from the flame-photometer (type B) followed closely by repeatability (type A).

For the extended uncertainty (U) of the method with a coverage factor k = 2, which gives a level of confidence of approximately 95% a value of ±10.18% was obtained.

REFERENCES

Çalişkan, B., & Çalişkan, A. C. (2019). Potassium Nutrition in Plants and Its Interactions with Other Nutrients in Hydroponic Culture. *Improvement of Quality in Fruits and Vegetables Through Hydroponic Nutrient Management*, 9.

Crusciol, C.A.C., Campos, M.d.C, Martello, J.M., Alves, C. J., Costa Nascimento, C. A., Reis Pereira, J. C. & Cantarella, H. (2020). Organomineral fertilizer as source of P and K for sugarcane. *Scientific Reports*, *10*. 5398 https://doi.org/10.1038/s41598-020-62315-1

De Oliveira, T. C., Rampazzo, R. T. Ferrao, M. F. & Pozebon, D. (2016). Method development and total uncertainty estimation for boron, sulfur and phosphorus determination in mineral fertilizer using ICP OES. *Jornal of the Brazilian Chemical Society,* 27(11). 2021−2033. .https://doi.org/10.5935/0103-5053.20160092

Ellison, S. L.R. & Williams A. (Eds.) (2012). *Eurachem/CITAC Guide CG4: Quantifying uncertainty in analytical measurement* (3rd ed.). https://www.eurachem.org

ISO 8466-1:1990 Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function

Kaya, C., Kirnak, H., Higgs, D. (2001). Enhancement of growth and normal growth parameters by foliar application of potassium and phosphorus in tomato cultivars grown at high (NaCl) salinity. J. *Plant Nutr. 24.* 357–367.

Khor, L. Y., & Zeller, M. (2014). Inaccurate fertilizer content and its effect on the estimation of production functions. *China Economic Review*, *30*. 123−132.

Kumari, S., Chhillar, H., Chopra, P., Khanna, R. R., & Khan, M. I. R. (2021). Potassium: A track to develop salinity tolerant plants. *Plant Physiology and Biochemistry*, *167*. 1011−1023.

Liu, J., Zheng, M., Wang, C., Liang, C., Shen, Z., & Xu, K. (2020). A green method for the simultaneous recovery of phosphate and potassium from hydrolyzed urine as value-added fertilizer using wood waste. *Resources, Conservation and Recycling*, *157*. 104793.

Magnusson, B. & Örnemark, U. (Eds.) (2014). *Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics*, second edition. ISBN 978-91-87461-59-0. www.eurachem.org.

Magnusson, B., Naykki, T., Hovind, H., Krysell, M. & Sahlin, E. (2017). *Handbook for calculation of measurement uncertainty in environmental laboratories,* Nordtest Report TR 537 (ed. 4) 2017. Available from www.nordtest.info.

Marschner, H. Mineral Nutrition of Higher Plants. 2nd ed. London: Academic Press; 1995. ISBN: 9780124735439

Nieves-Cordones, M., Ródenas, R., Lara, A., Martínez, V., & Rubio, F. (2019). The combination of K+ deficiency with other environmental stresses: what is the outcome? *Physiologia plantarum*, *165*(2), 264−276.

Order no. 6 of January 6, 2004 for the approval of the regulation on the organization and functioning of the Interministerial Commission for the authorization of fertilizers in order to be included in the list of authorized fertilizers, with the mention RO-FERTILIZER, for use and marketing in Romania

Raposo, F. (2016). Evaluation of analytical calibration based on least-squares linear regression for instrumental techniques: A tutorial review. *TrAC Trends in Analytical Chemistry*, *77.* 167−185.

Regulation (EC) No 2003/2003 of the European Parliament and of Council of 13 October 2003 relating to fertilizer. (L 304, 21.11.2003, pp. 1-194). Official Journal of the European Union. (2003)

Romanian Standards Association - ASRO (2018). *General requirements for the competence of testing and calibration laboratories*. (SR EN ISO/IEC 17025:2018).

https://www.sherwood-scientific.com/products/model-410/