

## EVALUATION OF UNCERTAINTY FOR DETERMINATION OF IRON FROM ORGANO-MINERAL FERTILIZERS BY ATOMIC ABSORPTION SPECTROMETRY

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### Abstract

*Organo-mineral fertilizers trade has known a significant growth in the internal market. Also, the range of products in this category has greatly diversified in the last period. In order to ensure fair competition in the fertilizer market and to protect the interests of end - users, European Regulations imposed higher requirements regarding marketing and quality control of fertilizers. Thus, it is now a formal requirement for laboratories to introduce quality assurance measures to ensure that they are capable of and are providing data of the required quality. Such measures include: accreditation based on ISO 17025 or the use of validated methods of analysis. Among several parameters, evaluation of uncertainty plays an important role in method validation. This paper presents the evaluation of uncertainty for determination of iron in organo-mineral fertilizers by means of atomic absorption spectrometry. A complex organo-mineral fertilizer was used for analysis and uncertainty sources were identified and quantified for each step of the process: weighing, dilution, equipment calibration and measuring iron concentration. Relative expanded uncertainty was 9.62% and repeatability was the main component of the uncertainty budget.*

**Key words:** fertilizers, iron, uncertainty.

### INTRODUCTION

It is expected that in the next 40 years the demand for food will increase by over 60% as the global population will rise to 9.7 billion in 2050. The global population growth will increase the demand for agricultural and food production, thus leading to a rising dependence on fertilizer inputs. The technology progress around the world, which works with modern environmental issues, attracts attention to agriculture and makes the domain of fertilizers technology the cornerstone for industrial development. The fertilizer market was valued at USD 155.80 billion in 2019, and it is estimated to register a CAGR of 3.8% by 2025. In the last period, organic and organo-mineral fertilizers trade have known a significant growth in the international market and the range of products in this category has greatly diversified (Lee, 2011; Mordor Intelligence, 2020).

Organo-mineral fertilizer can be defined as "a fertilizer obtained by blending, chemical reaction, granulation or dissolution in water of inorganic fertilizers having a declarable content

of one or more primary nutrients with organic fertilizers or soil improver" (Antille et al., 2013).

The use of organo-mineral fertilizers in agriculture is in accordance with the concept of sustainable intensification of agriculture. The definition of "sustainable agriculture" originates back in the USA in the early 1980s, indicating a way of farming that should mimic natural ecosystems (Gomiero et al., 2011). In the last years, a concept called "sustainable intensification" has been discussed, meaning producing more food from the same area of land while reducing the environmental impacts (Godfray et al., 2010).

It is reported by various authors that organo-mineral fertilizers give similar or higher yield responses as compared to conventional fertilizers for diverse crops: wheat, maize, barley, oil seed rape, pepper, amaranthus (Ailincăi et al., 2008; Akanni et al., 2011; Ayeni et al., 2012; Deeks et al., 2013). One of the most important features of using organo-mineral fertilizers is the "slow release" effect: mineral components are protected by the

binding and absorption of organic components which results in a more gradual release of nutrient to the soil and the reduction of nutrient losses to the environment (Kominoko et al., 2017).

With Romania's admission to the European Union, the national legislation on the regulation of marketing and quality control of fertilizers has been aligned with Community legislation. The higher requirements imposed by European Regulations are intended to ensure fair competition in the fertilizer market, to protect the interests of end - users, as well as to reduce the negative effects of these products on the environment. Among the measures for national implementation of the provisions of EU regulations are those relating to the organization of quality control of fertilizers activities by authorized laboratories, accredited by the national accreditation body (RENAR) according to ISO 17025. Thus, the laboratories are formally required by the mentioned standard to introduce in their management system measures for quality assurance, by which to demonstrate that they are able to provide analytical results of the quality required by customers or regulatory requirements (Grigore et al., 2011).

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). Uncertainty is a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand (Ellison & Williams, 2012).

Measuring uncertainty is a comprehensive parameter covering all sources of error and thus more than method validation alone. In practice, data from method validation and collaborative studies form the basis for measuring uncertainty evaluation. An analytical result must always be accompanied by an uncertainty statement. The interpretation and the use of any measurement fully depend on the uncertainty (at a stated level of confidence) associated with it (Taverniers, 2004).

This paper describes a method to evaluate measurement uncertainty for iron determination in organo-mineral fertilizers by flame atomic absorption spectrometry technique.

## MATERIALS AND METHODS

### Reagents

All reagents used were supplied by Merck (Darmstadt, Germany) and were of analytical purity: hydrochloric acid 37% HCl,  $c(\text{HCl}) = 12 \text{ mol/l}$ , nitric acid 65%,  $c(\text{HNO}_3) = 14.3 \text{ mol/l}$ , and lanthanum chloride heptahydrate ( $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ). CertiPUR® standard solution 1000 mg/l Fe was used for calibration curve. Ultra-pure water was used to prepare all solutions.

### Equipment

Determination of iron was performed using an atomic absorption spectrometer (AAS) Thermo Electron iCE 3300 (UK) with a hollow cathode lamp as radiation source, a deuterium lamp as background correction and air-acetylene flame. The working parameters are listed in Table 1. Ultra-pure water was obtained using a water purification system Evoqua (Germany).

Table 1. Working parameters for AAS

Parameter	Iron (Fe)
Wave length (nm)	248.3
Lamp current (mA)	15
Acetylene/air flow (L/h)	1.2
Burner (mm)	100

### Procedure

A complex NPK organo-mineral fertilizer was used for analysis. 2 g of the sample were weighted and quantitatively transferred to the reaction vessels. The test portions were moistened with about 0.5 ml to 1 ml of water and then, while mixing, 14 ml of HCl 37% and 4.7 ml of HNO<sub>3</sub> 65% were added. The reaction vessels were placed to the heating device until complete mineralization. After cooling, samples were transferred quantitatively into a 100 ml volumetric flask and diluted to the mark with ultra-pure water. Test solutions were filtered using ash-free filter paper. 20 ml of the sample extract were pipetted into a 100 ml volumetric flask, then 10 ml of diluted HNO<sub>3</sub> (5 mol/L) and 10 ml of lanthanum solution (10 g/L) were added. The flasks were filled to the mark with ultra-pure water, mixed well and

the solutions used for measurement. A blank test solution was prepared following the same procedure as for sample.

#### Calibration curve

In order to obtain the stock solution 10 ml of standard were pipetted into a 100 ml volumetric flask. The flask was filled to the mark with ultra-pure water. Adequate aliquots of standard solution were diluted with nitric acid solution (0.5 mol/l) to obtain 6 concentrations levels (0.5; 1.0; 1.5; 2.0; 2.5, and 3.0 mg/L Fe) and a squared correlation coefficient  $r^2 > 0.9990$  was considered acceptable.

#### Evaluation of uncertainty

The steps involved in evaluation of uncertainty are: specifying the measurand, identifying the uncertainty sources, quantifying the uncertainty components, and calculating the combined uncertainty.

#### Identification of the uncertainty sources

The measurand is the concentration of iron extracted from the complex fertilizer according to the procedure shown above.

$$c(Fe) = \frac{c_0 \times V_{100} \times d \times 10^{-4}}{m_s} \times rep \quad (\%) \quad (1)$$

Where:

$c_0$  – concentration of iron in the aliquot solution (mg/l),

$V_{100}$  – volume of the extraction solution (ml),

$d$  – dilution factor,

$m_s$  – mass of the sample (g)

rep – repeatability (the repeatability estimate is treated as a relative effect; rep=1).

The relevant sources of uncertainty were identified by constructing a cause-and-effect diagram (Figure 1). The main cause branches represent the parameters controlling the result as shown in Eq. 1.

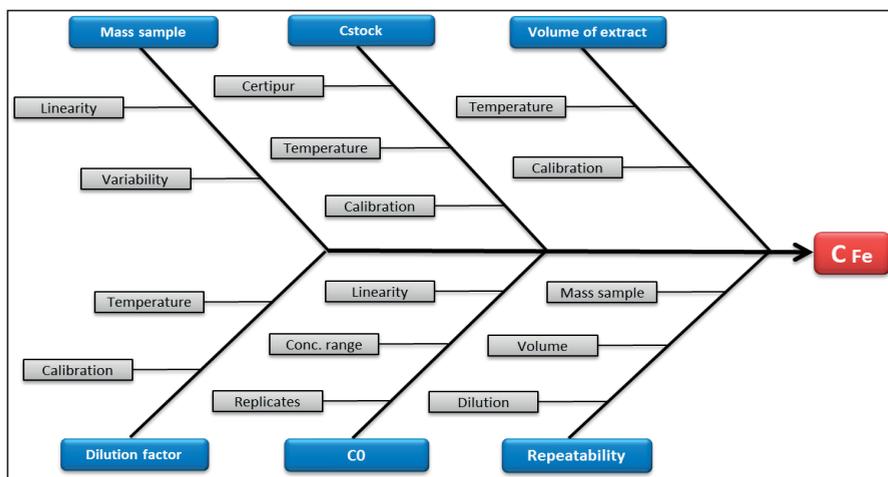


Figure 1. Cause-and-effect diagram for iron determination from organo-mineral fertilizers by AAS

## RESULTS AND DISCUSSIONS

#### Quantification of the uncertainty sources

Quantification of the uncertainty sources is done by using experimental data and standing data such as calibration certificates and reference materials certificates.

#### Mass of the sample, $m_s$

The uncertainty associated with the mass of organo-mineral fertilizer sample arises from the balance linearity and standard deviations of control charts (data obtained from verification of the balance using standard weights of 10 g and 50 g). The calibration certificate of the

balance quotes  $\pm 0.0003$  g for the linearity. Considering a rectangular distribution, the balance linearity contribution is 0.00017 g. The contribution from the balance linearity has to be counted twice, once for the tare and once for the gross weight, because each is an independent observation and the linearity effects are not correlated. The uncertainty associated with the mass of the sample is calculated accordingly:

$$u(m_s) = \sqrt{2 \times 0.00017^2 + 0.0002^2 + 0.0003^2}$$

$$\Rightarrow u(m_s) = 0.00044 \text{ g}$$

### Stock solution, $c_{stock}$

The uncertainty from stock solution depends upon the uncertainty of standard solution and volume. According to the supplier's certificate, concentration of the standard solution was  $984 \pm 4$  mg/kg. Assuming a normal distribution, the standard uncertainty of Certipur solution is  $u(c_{certipur}) = 2$  mg/kg.

The uncertainty associated with the volume has repeatability, calibration, and temperature as major influences. The repeatability is being taken into account via the combined repeatability term for the experiment. The calibration certificates quote volumes for the flask of  $100 \text{ ml} \pm 0.030 \text{ ml}$  and for the pipette of  $10 \text{ ml} \pm 0.023 \text{ ml}$  measured at a temperature of  $20^\circ\text{C}$ . The standard uncertainties are calculated assuming a normal distribution:  $u(V_{c100}) = 0.0150 \text{ ml}$  and  $u(V_{c10}) = 0.0115 \text{ ml}$ . According to the calibration certificates, the flask and the pipette have been calibrated at a temperature of  $20^\circ\text{C}$ , whereas the laboratory temperature varies between the limits of  $\pm 4^\circ\text{C}$ . The coefficient of volume expansion for water is  $2.1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ , which leads to a volume variation of  $\pm 0.0840^\circ\text{C}$  and  $\pm 0.0084^\circ\text{C}$  respectively. The uncertainties are calculated using the assumption of a rectangular distribution for the temperature variation:  $u(V_{t100}) = 0.0489 \text{ ml}$  and  $u(V_{t10}) = 0.0049 \text{ ml}$ . The two contributions are combined to give the standard uncertainties of the volumes:  $u(V_{100}) = 0.0508 \text{ ml}$  and  $u(V_{10}) = 0.0124 \text{ ml}$ .

Combining the intermediate standard uncertainties above calculated, the standard uncertainty of the iron stock solution is given by Eq. 2.

$$\frac{u(c_{stock})}{c_{stock}} = \sqrt{\left(\frac{u(c_{certipur})}{c_{certipur}}\right)^2 + \left(\frac{u(V_{100})}{V_{100}}\right)^2 + \left(\frac{u(V_{10})}{V_{10}}\right)^2} \quad (2)$$

$$\frac{u(c_{stock})}{100} = \sqrt{\left(\frac{2}{984}\right)^2 + \left(\frac{0.0508}{100}\right)^2 + \left(\frac{0.0124}{10}\right)^2}$$

$$\Rightarrow u(c_{stock}) = 0.2437 \text{ mg/l}$$

### Dilution factor, $d$

The relative uncertainty from the dilution factor is  $u(d) = 0.00086$  and was calculated combining the relative uncertainties associated with the volume for the 100 ml flask and 20 ml pipette.

The calculation of the uncertainty associated with the volume is previously described.

### Concentration of the aliquot solution, $c_0$

The calibration curve was manually prepared. For this purpose, six calibration standards, with concentrations of 0.5 mg/L, 1.0 mg/L, 1.5 mg/L, 2.0 mg/L, 2.5 mg/L and 3.0 mg/L, were prepared from a 1000 mg/L iron reference standard. The usual uncertainty calculation procedures for  $c_0$  only reflect the uncertainty due to random variation in the absorbance and not the uncertainty of the calibration standards, nor the inevitable correlations induced by successive dilution from the same stock which are sufficiently small to be neglected (Ellison and Williams, 2012).

The six calibration standards were measured three times each providing the results in Table 2. The results of the linear least square fit are  $B_1 = 0.12347$ ,  $B_0 = 0.00927$  with a correlation coefficient of 0.9995. The sample solution was measured three times also, leading to a concentration  $c(0)$  of 1.53 mg/L.

Table 2. Calibration results

Concentration (mg/L)	Absorbance (replicates)		
	1	2	3
0.5	0.067	0.068	0.069
1.0	0.133	0.134	0.133
1.5	0.196	0.198	0.196
2.0	0.258	0.261	0.259
2.5	0.317	0.317	0.319
3.0	0.377	0.377	0.377

The uncertainty of iron concentration  $u(c_0)$  is given by Eq. 3, with the residual standard deviation  $S$ , given by Eq. 4 and  $S_{xx}$  given by Eq. 5.

$$u(c_0) = \frac{S}{B_1} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{S_{xx}}} \quad (3)$$

$$S = \sqrt{\frac{\sum_{j=1}^n [A_j - (B_0 + B_1 \times c_j)]^2}{n - 2}} \quad (4)$$

$$\Rightarrow S = 0.00279 \text{ mg/l}$$

$$S_{xx} = \sum_{j=1}^n (c_j - \bar{c})^2 = 4.38 \text{ mg/L} \quad (5)$$

$$u(c_0) = \frac{0.00279}{0.12347} \sqrt{\frac{1}{3} + \frac{1}{18} + \frac{(1.53 - 1.75)^2}{4.38}}$$

$$\Rightarrow u(c_0) = 0.0143 \text{ mg/l}$$

Where:

$A_j$  –  $i^{\text{th}}$  measurement of absorbance,

$B_0$  – intercept,

$B_1$  – slope,

$p$  – number of measurements to determine  $c_0$ ,

$n$  – number of measurements for the calibration,

$c_0$  – determined iron concentration of the aliquot solution,

$\bar{c}$  – mean value of the different calibration standards ( $n$  number of measurements),

$i$  – index for the number of calibration standards,

$j$  – index for the number of measurements to obtain the calibration curve.

*Repeatability, rep*

The repeatability was determined using ten repeated measurements of the organo-mineral fertilizer sample which lead to an average of 0.0395% Fe and a standard deviation of 0.0018%. The value of the relative standard deviation,  $RSD = 4.67\%$  can be used directly for the calculation of the combined standard uncertainty.

*Calculating the combined standard uncertainty*

All the intermediate values of the measurement and their standard uncertainties are presented in Table 3.

Table 3. Intermediate values and uncertainties for determination of iron from organo-mineral fertilizers

Description	Value	Standard uncertainty $u(x)$	Relative standard uncertainty $u(x)/x$
Mass of the sample, $m_s$	2 g	0.00044 g	0.00022
Stock solution, $c_{stock}$	100 mg/L	0.2437 mg/L	0.00244
Volume of extracted solution, $V_{100}$	100 ml	0.0508 ml	0.00051
Volume, $V_{100}$	100 ml	0.0508 ml	0.00051
Volume, $V_{20}$	20 ml	0.0139 ml	0.00069
Dilution, $d$			0.00086
Concentration of the aliquot solution, $c_0$	1.53 mg/L	0.0143 mg/L	0.00936
Repeatability, rep	1	0.04670	0.04670

In order to calculate the combined standard uncertainty, the standard uncertainties of each component are used as follows (Eq. 6):

$$\frac{u(c_{Fe})}{c_{Fe}} = \sqrt{\left(\frac{u(c_{ms})}{m_s}\right)^2 + \left(\frac{u(Vc_{stock})}{c_{stock}}\right)^2 + \left(\frac{u(V_{100})}{V_{100}}\right)^2 + u(d)^2 + \left(\frac{u(c_0)}{c_0}\right)^2 + u(rep)^2} \quad (6)$$

$$\frac{u(c_{Fe})}{0.0395} = \sqrt{0.00022^2 + 0.00244^2 + 0.00051^2 + 0.00086^2 + 0.00936^2 + 0.04670^2}$$

$$\Rightarrow u(c_{Fe}) = 0.0019\%$$

The expanded uncertainty  $U_{Fe}$  is calculated by multiplying the combined standard uncertainty by a coverage factor  $k = 2$ , which gives a level of confidence of approximately 95% (Eq. 7). Thus, the content of iron in the organo-mineral fertilizer is  $(0.0395 \pm 0.0038)\%$ . Relative expanded uncertainty is 9.62%.

$$U_{Fe} = 2 \times u(c_{Fe}) = 2 \times 0.0019 = 0.0038\% \quad (7)$$

Figure 2 illustrates the contribution of each component to the uncertainty budget. The contribution of the uncertainty of repeatability is by far the largest (77.73%) followed by the concentration of iron in the aliquot solution (15.58%).

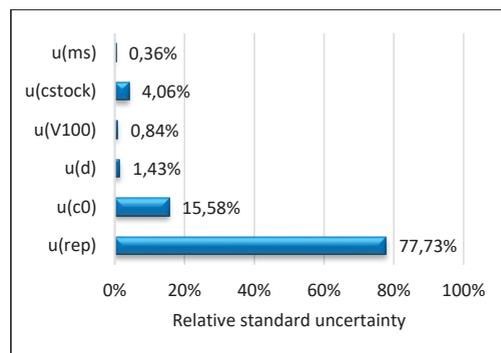


Figure 2. Uncertainty contributions for determination of iron from organo-mineral fertilizers

## CONCLUSIONS

Fertilizer production is a complex and demanding process. As regulatory requirements shift, and awareness of environment issues is growing, the focus on quality control of fertilizers is more intense than ever before. Measuring uncertainty is a key indicator for both fitness-for-purpose of a method and constant reliability of analytical results achieved in a laboratory.

Application of cause-and-effect analysis was used to evaluate the measurement uncertainty

for iron determination in organo-mineral fertilizers by means of atomic absorption spectrometry. The content of iron in the analysed organo-mineral fertilizer sample is  $(0.0395 \pm 0.0038)\%$ . The assessment of various steps of the measurement shows that repeatability, with a contribution of 77.73% was the main component of the uncertainty budget.

## ACKNOWLEDGEMENTS

This work was supported by ADER Program, Contract ADER 144 /2019, Project "Identification, evaluation, testing, development and validation of methods of analysis for nutrients and contaminants from inputs used in organic farming".

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