QUALITY CONTROL OF FERTILISERS - VALIDATION OF THE MICRO-NUTRIENTS ANALYSIS FROM THE INORGANIC FERTILISERS

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Abstract: *Romania's accession to the European Union imposed the alignment of national legislation concerning the fertilisers with the European legislation. Thus, the internal normative acts regulating the trading of fertilisers and their quality control have been harmonized with the European ones by taking-up the full EC Regulation No 2003/2003. The official control of the conformity of the fertilizers to the requirements of the EC Regulation regarding the quality and composition is regulated by law no 238 from 07.12.2010 and performed by laboratories operating under SR EN ISO 17025:2005 standard, accredited by the national accreditation body – RENAR and notified to the European Commission. Thus, laboratories are required to appropriate measures to ensure that they are able to deliver the expected quality of the results, demonstrating their competence. This paper presents the validation of the iron analysis from inorganic fertilisers. Extraction and determination of iron by atomic absorption spectrometry are made under the methods 9.1. and 9.4. from Annex III of the EC Regulation No 2003/2003in the Laboratory for Testing and Quality Control of Fertilizers (accreditation certificate LI 673/2008) within the National Research and Development Institute for Soil Science, Agrochemistry and Environment Protection – RISSA Bucharest. The values obtained from the laboratory experiments, estimated by statistical calculation show that the results are within the confidence limits for the probability of 95%, both in terms of repeatability and exactness, thus the method is validated.*

Key words: *fertilizers, micro-nutrients, method validation*

INTRODUCTION

Romania's accession to the European Union imposed the alignment of national legislation concerning the fertilisers with the European legislation. Thus, the internal normative acts regulating the trading of fertilisers and their quality control have been harmonized with the European ones by taking-up the full EC Regulation No 2003/2003. The EC Regulation was implemented through a series of national legislative measures, including the organization of an official inspection in order to control the EC marked fertilisers.

The requirements imposed by the EC Regulation No 2003/2003 are meant to ensure fair competition on the fertiliser market, to protect the farmer's interests and to diminish the negative effects of these products on the environment.

The range of fertilisers with micro-nutrients is a wide one. Micro-nutrients: B, Co, Cu, Fe, Mn, Mo, Zn, essential to the plant growth, are needed in small amounts comparing to primary and secondary nutrients. Annex IE of the EC Regulation No 2003/2003 presents the list of types of EC inorganic micro-nutrients fertilisers:

- fertilisers containing only one micro-nutrient;
- fertilisers containing primary and/or secondary nutrients with micro-nutrients applied to the soil;
- fertilisers containing primary and/or secondary nutrients with micro-nutrients for leaf spray.

Minimum micro-nutrients contents of these fertilizers are given in Section E2 of Annex I of the EC Regulation. The tolerance allowed in respect of the declared micro-nutrient content shall be:

- 0.4% in absolute terms for a content of more than 2%;
- one fifth of the declared value for a content not exceeding 2%.

The official control of the conformity of the fertilizers to the requirements of the EC Regulation regarding the quality and composition is regulated by law no 238 from 07.12.2010 and performed by laboratories operating under SR EN ISO 17025:2005 standard, accredited by the national accreditation body – RENAR and notified to the European Commission. Thus, laboratories are required to appropriate measures to ensure that they are able to deliver the expected quality of the results, demonstrating their competence:

- use of validated analytical methods;
- use of internal quality control procedures (use of reference materials, control charts);
- participation in laboratory proficiency testing schemes.

Method validation is a tool used to demonstrate that a method is fit for purpose and its performance characteristics are capable of producing results in line with the requirements of the analytical problems. The depth of the validation depends on the maturity and the scope of the method. There is a distinction between:

- new methods;
- standardized methods;
- methods developed/validated already, but were changes were made.

Standardized methods are deemed to have been validated, but laboratories should verify that their application is correct. Organizing a validation action leads to clear conclusions on the existence of appropriate equipment and trained, experienced personnel.

Validation of a method involves the evaluation of performance characteristics such us: precision, trueness, linear response range, limit of detection, measurement uncertainty.

MATERIAL AND METHODS

This paper presents the validation of the iron analysis from inorganic fertilisers. Extraction and determination of iron by atomic absorption spectrometry are made under the methods 9.1. and 9.4. from Annex III of the EC Regulation No 2003/2003in the Laboratory for Testing and Quality Control of Fertilizers (accreditation certificate LI 673/2008) within the National Research and Development Institute for Soil Science, Agrochemistry and Environment Protection – RISSA Bucharest.

Apparatus: atomic absorption spectrometer Thermo Fisher Scientific, ICE 3300.

Reagents: iron standard solution 1000 mg/L (CertiPUR, Merck), hydrochloric acid 37% (Merck), certified reference material, superphosphate – BCR 033.

By diluting the standard solution with 0.5 mol/L hydrochloric acid were prepared six calibration solutions (in five replicates) within the range 0.5 – 3.0 mg/L Fe. These calibration solutions were used for the evaluation of the linearity. Evaluation of the performance parameters (precision, trueness, recovery) was performed using a certified reference material worked in ten replicates. For determining the detection limit and the quantification limit were prepared ten blank samples by repeating the whole procedure from the extraction omitting only the test sample of certified material.

RESULTS AND DISCUSSIONS

The values obtained from laboratory experiments, estimated by statistical calculation, are summarized in Table 1. The correlation coefficient of the calibration curve is 0.9992 and by

comparing the calculated value of F = 6.77 with the theoretical value F (0.05, 1, 28) = 4.20 the linear model is confirmed. The calibration curve is presented in Figure 1.

Table 1

Parameters of the calibration curve and evaluation of the detection and quantification limits

Parameter	Value
Working range	0.1 – 3.0 mg Fe/L
Curve ecuation	y = 0.0139 + 0.1189·x
Correlation coefficient	R^2 = 0,9992
Slope	b = 0.1190 absorbance units/mgL^{-1}
Intercept	b_0 = 0,0139
Average of blank samples	0.0534 mg Fe/L
Standard deviation (s_{bl})	0.0055 mg Fe/L
Detection limit ($3 \cdot s_{bl}$)	0.0699 mg Fe/L
Quantification limit ($10 \cdot s_{bl}$)	0.1085 mg Fe/L

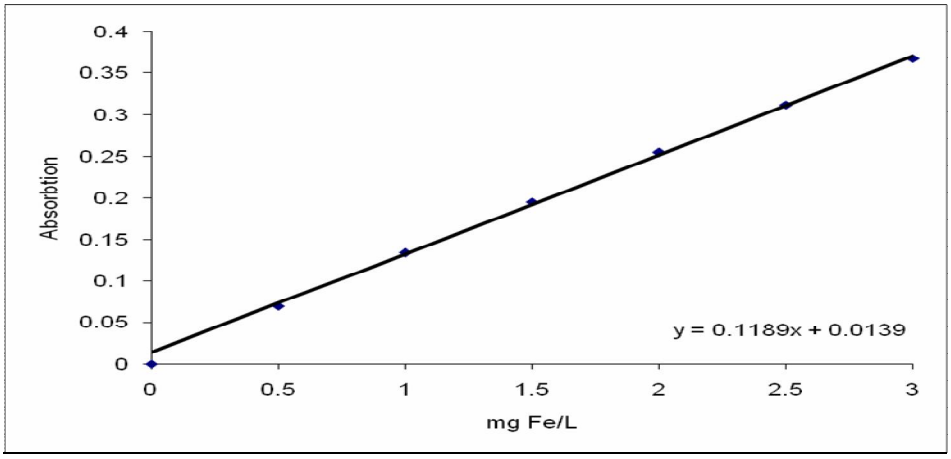

Figure 1. The calibration curve used for the analysis of iron

The evaluation of the precision of the method is obtained by comparing the laboratory standard deviation (s) with the standard deviation (sw) from the certificate accompanying the reference material. The following ratios are calculated:

$$\chi^2_c=(s/S_w)^2; \quad \chi^2_t= \chi^2_{0.95;\,9}/9 \qquad (1)$$

The χ^2_c value obtained is compared with the theoretical value of $\chi^2_{0.95;\,9}$ which corresponds to a probability of 95% and to nine degrees of freedom. $\chi^2_c < \chi^2_t$, (0.33 < 1.88) so the method has the adequate precision.

The evaluation of the truness of the method is made by comparing the average of the ten results obtained in the laboratory with the certificate value of the reference material.

$$\left|\overline{x} - m\right| < 2 \cdot S_B \qquad (2)$$

Relation (2) is satisfied (0.01 < 0.44) so the measurement procedure has the required accuracy. The values of the performance characteristics used to evaluate the precision and the

trueness are presented in Table 2.

Table 2

Evaluation of the precision and the truenessof the method
(according to ISO GUIDE 33:2000)

Values according to the BCR 033 certificate no 6808	Values obtained in the laboratory
Certified value: m = 3,98 mgFe_2O_3/g	Averege: $\bar{x}$ = 3,99 mgFe_2O_3/g
Repetability: s_w = 0,06 mgFe_2O_3/g	Standard deviation: s = 0,034 mgFe_2O_3/g
Between labs standard deviation: s_B = 0,22 mgFe_2O_3/g	Recovery: 100,32%
Precision evaluation	$\chi^2_c = (0{,}034/0{,}06)^2 = 0{,}33$ $\chi^2_t = 16{,}9/9 = 1{,}88$
Trueness evaluation	$\lvert 3{,}98 - 3{,}99 \rvert < 2 \cdot 0{,}22$ $0{,}01 < 0{,}44$

CONCLUSIONS

The extraction and the analysis of iron from inorganic fertilisers have been validated: the results are within the confidence limits for the probability of 95%, both in terms of repeatability and exactness.

The working range is linear from 0.1 to 3.0 mg/L Fe, allowing the analysis of a broad spectrum of concentrations.

Organizing the validation action demonstrated that the method is fit for purpose and the laboratory has both trained, experienced analysts and suitable equipment.

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