Annex D.5

Inorganic fertilizers — Determination of the total K_2O content

Draft method

1 Scope

This document specifies two different methods (Method A and B) for the determination of the content of potassium (expressed as K_2O) in inorganic fertilizers. Method A specifies a gravimetric method. Method B specifies the method using inductively coupled plasma optical emission spectrometry (ICP-OES).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN 12944-1, *Fertilizers and liming materials — Vocabulary — Part 1: General terms*

EN 12944-2, *Fertilizers and liming materials — Vocabulary — Part 2: Terms relating to fertilizers*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

4.1 Method A: Gravimetric method

The potassium in the homogenized sample to be analysed is dissolved in diluted hydrochloric acid solution. After eliminating or fixing the substances that might interfere with the quantitative determination, the potassium is precipitated in a slightly alkaline medium in the form of potassium tetraphenylborate (KTPB).

4.2 Method B: ICP-OES method

The potassium in the homogenized sample to be analysed is dissolved in diluted hydrochloric acid solution. If undissolved material remains, filtering is needed. The mass concentration of potassium is determined by optical emission spectrometry with inductively coupled plasma (ICP-OES).

ICP-OES instruments using sequential or simultaneous optical systems and axial, radial or dual viewing of the plasma may be used. The quantification of potassium is achieved by using linear calibration functions.

5 Sampling and sample preparation

5.1 Sampling

Sampling is not part of the method specified in this document. A recommended sampling method is given in EN 1482-1 [2]. A recommended sampling method for sampling of static heaps is given in EN 1482-3 [3].

5.2 Sample preparation

Sample preparation, including sample division shall be performed according to EN 1482-2. Grinding of the sample is recommended for homogeneity reasons.

5.3 Preparation of the test portion and the sample solution

Weigh, to the nearest 0,001 g, 10 g of the prepared sample (5 g for samples with an expected mass fraction of potassium oxide of more than 50%). Transfer this test portion to a 600 ml beaker. In a fume cupboard add slowly 300 ml of the hydrochloric acid solution (6.1.1), cover the beaker with a watch glass and bring to the boil and continue boiling for 30 min. Allow to cool. Transfer quantitatively into a 1 000 ml graduated flask, make up the volume with the hydrochloric acid solution (6.1.1), mix well and filter into a dry beaker. Discard the first 50 ml of the filtrate.

6 Method A: Gravimetric method

6.1 Reagents

Use only reagents of recognized analytical grade.

The electrical conductivity of distilled or demineralized water used in the analysis shall at least be < 0,5 mS/m (at 25°C).

6.1.1 Hydrochloric acid, diluted solution 1 + 10 volume fraction.

In a fume cupboard, add 200,0 ml of concentrated hydrochloric acid (ρ_{20} = 1,18 g/ml) to about 1 600 ml of water and cool. Dilute the solution with water to 2 000 ml and mix.

6.1.2 Formaldehyde, clear formaldehyde solution with a mass fraction of 25 % to 35 % formaldehyde.

6.1.3 Potassium chloride, analytical grade (100 % purity) w_{K2O} = 63,18 %, dried at (200 ± 10) °C for 2 h.

6.1.4 Sodium hydroxide solution, c = 10 mol/l.

Care should be taken to ensure that only potassium free sodium hydroxide is used.

Store the reagent in a plastics container.

6.1.5 Indicator solution

Dissolve 0,5 g of phenolphthalein in ethanol at 90 % and make the volume up to 100 ml.

6.1.6 EDTA solution

Dissolve 4 g of the dihydrated disodium salt of ethylenediaminetetraacetic acid in water in a 100 ml graduated flask. Make up to volume and mix.

Store the reagent in a plastics container.

6.1.7 STPB solution

Dissolve 32,5 g of sodium tetraphenylborate in 480 ml of water, add 2 ml of the sodium hydroxide solution (6.1.4) and 20 ml of a magnesium chloride solution (100 g of $MgCl_2 \cdot 6H_2O$ per litre).

Stir for 15 min and filter through a fine, ashless filter.

Store this reagent in a plastics container.

6.1.8 Liquid for washing

Dilute 20 ml of the STPB solution (6.1.7) to 1 000 ml with water.

6.2 Apparatus and equipment

Usual laboratory apparatus and, in particular, the following.

6.2.1 Graduated flasks, capacity 1 000 ml and 2 000 ml.

6.2.2 Pipettes, capacity 10 ml, 25 ml, and 50 ml.

6.2.3 Beakers, capacity 250 ml and 600 ml.

6.2.4 Measuring cylinder, capacity 500ml.

6.2.5 Filter crucibles, porosity 5 µm to 20 µm.

6.2.6 Boiling water (steam) bath.

6.2.7 Drying oven, regulated at 120 ± 10 °C.

6.2.8 Desiccator.

6.2.9 Analytical balance, precision ± 0,1 mg.

6.3 Procedure

6.3.1 Preparation of the aliquot part for precipitation

Transfer by pipette an aliquot part of the filtrate (5.3) containing 25 mg to 50 mg of potassium oxide (see table 1) and place it in a 250 ml beaker. If required, make up to 50 ml with water.

To remove any interference, add 25 ml of the EDTA solution (6.1.6), several drops of the phenolphthalein solution (6.1.5) and stir in, drop by drop, sodium hydroxide solution (5.4) until it turns red, then finally add a few more drops of sodium hydroxide to ensure an excess.

Boil gently for 15 min.

NOTE Where no ammoniacal nitrogen is present in the analysed sample there is no need to boil for 15 min.

If necessary, add water to make the volume up to 60 ml.

Bring the solution to the boil, remove the beaker from the heat and add 10 ml of formaldehyde (6.1.2). Add several drops of phenolphthalein and, if necessary, some more sodium hydroxide until a distinct red colour appears. Cover the beaker with a watch glass and place it on a boiling water (steam) bath for 15 min.

6.3.2 Weighing the crucible

Dry the filter crucible to a constant mass (about 15 min) in the oven at 120 °C.

Allow the crucible to cool in a desiccator and then weigh it (precision ± 0,1 mg).

6.3.3 Precipitation

Remove the beaker from the boiling water (steam) bath, stir in drop-by-drop 10 ml of the STPB solution (6.1.7). This addition should take about 2 min. Wait for at least 20 min (but no more than 30 min) before filtering.

6.3.4 Filtering and washing

Filter under vacuum into the weighed crucible, rinse the beaker with the liquid for washing (6.1.8), wash the precipitate three times with the liquid for washing (60 ml in all of the liquid for washing), and twice with 5 ml to 10 ml of water.

6.3.5 Drying and weighing

Wipe the outside of the crucible with a filter paper. Place the crucible with its contents in the oven for 1,5 h at 120 °C. Allow the crucible to cool in a desiccator to ambient temperature and weigh immediately.

6.3.6 Aliquot parts to be taken as samples and conversion factors

Table 1 — Aliquot parts and conversion factors

K_2O in the fertilizer %	**K in the fertilizer** %	**Sample for analysis** g	**Aliquot part to be taken as a sample for precipitation** ml	**Conversion factor F** $\frac{\%K_2O}{g\ KTPB}$	**Conversion factor F'** $\frac{\%K}{g\ KTPB}$
5 – 10	4,2 – 8,3	10	50	26,280	21,812
10 – 20	8,3 – 16,6	10	25	52,560	43,624
20 – 50	16,6 – 41,5	10	10	131,400	109,060
more than 50	more than 41,5	5	10	262,800	218,120

6.3.7 Blank test

For each series of determinations, carry out a blank test using only the reagents in the proportions used in the analysis and allow for this when calculating the final result.

6.3.8 Control test

In order to obtain a control for the method of analysis, carry out a determination on an aliquot part of a solution of potassium chloride dissolved in diluted hydrochloric acid (6.1.1), containing at the most 40 mg of K_2O.

6.4 Calculation and expression of the result

6.4.1 Dilution according to table 1

Calculate the K_2O content, w_{K_2O}, as mass fraction in percent of the fertilizer according to Formula (1):

$$w_{K_2O} = (m_1 - m_2) \times F \quad (1)$$

Calculate the K content, w_K, as mass fraction in percent of the fertilizer according to Formula (2):

$$w_K = (m_1 - m_2) \times F' \quad (2)$$

where

m_1 is the mass of the precipitate from the sample, in g;

m_2 is the mass of the precipitate from the blank, in g;

F and F' conversion factors (see Table 1).

6.4.2 Dilution different from table 1

Calculate the K_2O content, w_{K_2O} , as mass fraction in percent of the fertilizer according to Formula (3):

$$w_{K_2O} = \frac{(m_1 - m_2) \times \mathbf{0{,}1314} \times D \times 100}{m} \quad (3)$$

Calculate the K content, wK, as mass fraction in percent of the fertilizer according to Formula (4):

$$w_K = \frac{(m_1 - m_2) \times \mathbf{0{,}109} \times D \times 100}{m} \quad (4)$$

where

m_1 is the mass of the precipitate from the sample, in g;

m_2 is the mass of the precipitate from the blank, in g;

0,1314 - conversion factor, KTPB into K_2O;

0,109 - conversion factor, KTPB into K;

D is the dilution factor;

m is the mass of the sample for analysis (test portion), in g.

7 Method B: ICP-OES method

7.1 Reagents

7.1.1 General

All reagents, excluding acids, but including water shall be of recognized analytical grade and they shall have negligible concentration of the element to be determined if compared to the lowest concentration of that element in the sample solution. Regarding the quality of water used for analytical work involving trace analysis, the electrical conductivity shall at least be < 0,2 mS/m (at 25°C).

7.1.2 Nitric acid, substance concentration $c(HNO_3) \approx 14{,}3$ mol/l, $\rho \approx 1{,}4$ g/ml; trace metal grade or similar purity grade.

7.1.3 Potassium chloride (KCl), trace metal grade or similar purity grade, dried at least at (250 ± 10)°C.

7.1.4 Potassium sulphate (K_2SO_4), trace metal grade or similar purity grade, dried at least at (250 ± 10) °C.

7.1.5 Potassium nitrate (KNO_3), analytical grade

7.1.6 Sodium sulphate (Na_2SO_4) , trace metal grade or similar purity grade, dried at least at (250 ± 10) °C.

7.1.7 Sodium chloride (NaCl) , trace metal grade or similar purity grade, dried at least at (250 ± 10) °C.

7.1.8 Magnesium sulphate heptahydrate ($MgSO_4 \cdot 7\ H_2O$), trace metal grade or similar purity grade, dried at least at (250 ± 10) °C.

7.1.9 Di-Ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), analytical grade.

7.1.10 Ammonium sulphate ($(NH_4)_2SO_4$), analytical grade.

7.1.11 Calcium sulphate dihydrate ($CaSO_4 \cdot 2\ H_2O$), analytical grade.

7.1.12 Standard stock solutions for magnesium, calcium, sodium, and phosphate, concentration of 10 000 mg/l (10 g/l) for each element.

Both single-element stock solutions and multi-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered. Alternatively, the stock solutions may be prepared by the dissolution of high purity salts.

NOTE The standard stock solutions for magnesium and calcium should have been made from $Mg(NO_3)_2$ and $Ca(NO_3)_2$, respectively.

7.1.13 Standard stock solutions for lithium, concentration of 1 000 mg/l (1 g/l).

Single-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered. Alternatively, the stock solutions may be prepared by the dissolution of high purity salts.

7.1.14 Argon, purity 99,995 % or better**.**

7.1.15 Calibration stock solution I (including matrix modifier for universal application)

Transfer 11,677 g of Na_2SO_4 (7.1.6), 300 ml of PO_4 standard stock solution 10 g/l (7.1.12), and 10 ml of nitric acid (7.1.2) into a 1 000 ml graduated flask, dissolve with water, temper, fill up to the mark, and homogenise.

NOTE The calibration stock solutions are needed to ensure universal use of the calibration for as many inorganic fertilizers as possible. The composition of these solutions serves on the one hand as a matrix modifier and on the other hand to adjust the salt content in the ICP-OES measurement.

7.1.16 Calibration stock solution II (including matrix modifier for universal application)

Transfer 9,953 g of KCl (7.1.3), 200 ml of Mg standard stock solution 10 g/l (7.1.12), 100 ml of Ca standard stock solution 10 g/l (7.1.12), and 10 ml of nitric acid (7.1.2) into a 1 000 ml graduated flask, dissolve with water, temper, fill up to the mark, and homogenise.

7.1.17 Dilution solution

Transfer 5,0 ml of standard stock solution for Li 1 g/l (7.1.13) and 10 ml of nitric acid (7.1.2) into a 1 000 ml graduated flask, dissolve with water, temper, fill up to the mark, and homogenise.

NOTE Alternatively, a Y-piece on the nebuliser can be used for on-line dosing of the internal standard (Li). In this case the Li standard stock solution (7.1.13) should not be added to this dilution solution. To do so, the added Li solution concentration in the spray chamber (and plasma) should be chosen according to the intensity of the K signal. Also, it requires a very good, proven long-term precision of the on-line dosing method.

7.1.18 Control sample MOP (muriate of potash)

Transfer 9,550 g of KCl (7.1.3), 0,350 g of NaCl (7.1.7) and 0,200 g of $MgSO_4 \cdot 7\ H_2O$ (7.1.8) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (60,33 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

7.1.19 Control sample SOP (sulphate of potash)

Transfer 9,600 g of K_2SO_4 (7.1.4), 20 mg of NaCl (7.1.7), 50 mg of $MgSO_4 \cdot 7\ H_2O$ (7.1.8) and 3 ml Ca standard stock solution 10 g/l (7.1.12) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (51,91 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

7.1.20 Control sample NOP (nitrate of potash)

Transfer 10,000 g of KNO_3 (7.1.5) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (46,58 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

7.1.21 Control sample NPK

Transfer 2,6905 g of KCl (7.1.3), 2,2344 g of $(NH_4)_2HPO_4$ (7.1.9), 3,8319 g of $(NH_4)_2SO_4$ (7.1.10), 20 ml of Mg standard stock solution 10 g/l (7.1.12), 30 ml of Ca standard stock solution 10 g/l (7.1.12) and 2 ml of Na standard stock solution 10 g/l (7.1.12) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (17,00 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, the fertilizer.

7.1.22 Control sample Polyhalite

Transfer 2,553 0 g of K_2SO_4 (7.1.4), 3,600 0 g of $MgSO_4 \cdot 7\ H_2O$ (7.1.8), and 4,050 0 g of $CaSO_4 \cdot 2\ H_2O$ (7.1.11) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 20 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (13,80 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

7.1.23 Fertilizer type standard MOP (muriate of potash)

Transfer 9,900 g of KCl (7.1.3), 0,350 g of $NaSO_4$ (7.1.6). 15 ml Mg standard stock solution 10 g/l (7.1.12), and 3 ml Ca standard stock solution 10 g/l (7.1.12) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (62,55 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

This fertilizer type standard is recommended to use for analysing fertilizers containing KCl as main component.

7.1.24 Fertilizer type standard SOP (sulphate of potash)

Transfer 9,430 g of K_2SO_4 (7.1.4), 102 mg of NaCl (7.1.7), 203 mg of $MgSO_4 \cdot 7\ H_2O$ (7.1.8) and 2 ml Ca standard stock solution 10 g/l (7.1.12) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (50,92 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

This fertilizer type standard is recommended to use for analysing fertilizers containing K_2SO_4 as main component.

7.1.25 Fertilizer type standard NPK

Transfer 2,500 g of KCl (7.1.3), 4,050 g of $(NH_4)_2HPO_4$ (7.1.9), 2,000 g of Na_2SO_4 (7.1.6), 20 ml of Mg standard stock solution 10 g/l (7.1.12), and 10 ml of Ca standard stock solution 10 g/l (7.1.12) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 10 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (15,79 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

This fertilizer type standard is recommended to use for analysing fertilizers containing N-, P-, and K-based compounds as main components.

7.1.26 Fertilizer type standard Polyhalite

Transfer 2,589 8 g of K_2SO_4 (7.1.4), 3,668 2 g of $MgSO_4 \cdot 7\ H_2O$ (7.1.8), and 4,080 9 g of $CaSO_4 \cdot 2\ H_2O$ (7.1.11) into a 1 000 ml graduated flask. Add approx. 500 ml of water, 20 ml of nitric acid (7.1.2) and mix until the salts are dissolved. Then fill up to the mark with water, temper, and homogenise.

w_{K2O} = (14,00 ± 0,18) %

where

w_{K2O} is the target mass fraction of K_2O, in %, of the fertilizer.

This fertilizer type standard is recommended to use for analysing fertilizers containing K_2SO_4 and $CaSO_4$ as component.

7.2 Apparatus and equipment

Usual laboratory glassware and equipment, in particular, the following.

7.2.1 Inductively coupled plasma optical emission spectrometer (ICP-OES).

WARNING – It is essential that the manufacturer's safety instructions are strictly observed when using this apparatus.

The ICP-OES instrument consists of a sample introduction system, the plasma as an excitation source, an optical system, a detector, and a computer with suitable software. The sample is transported by the introduction system (rotation tube pump, nebuliser, and a spray chamber) to the plasma torch. Around the torch a cooled RF coil is placed. A frequency of 27 MHz to 56 MHz with a power of 600 W to 2 500 W is usually used. The emission from the plasma can be observed either from the side (radial) or from the torch central symmetrical axis (axial). Axial viewing gives more signal intensity due to the increased observation path length of the normal analytical zone of the plasma, but an increase of interference is also commonly observed. Spectral lines are measured and registered either in a sequential or a simultaneous manner.

It is recommended to use radial plasmas, but when using axial plasmas, the "easily ionisable element effect" (the influencing of easily ionisable elements through calibration in the presence of other easily ionisable elements in variable concentrations) shall be considered – for alkali elements e.g. by addition of CsCl solution.

7.2.2 Dilution automate (diluter or dispenser) or other suitable instruments for dilution of solutions, e.g. pipettes.

7.2.3 Graduated flask, capacity 500 ml and 1 000 ml.

7.3 Procedure

7.3.1 General

The high precision and accuracy of the test method necessary for determining high contents of K_2O in fertilizers is achieved through the following measures:

- Optimised equipment settings according to instrument manufacturer. To ensures this criterion it is recommended to perform a performance check according to the manufacture specifications prior to the analyses.
- Simultaneous measurement of the signal intensity of analyte and suitable internal standard, here Li.
- Matrix matched calibration.

- Identical treatment of samples and calibration solutions during sample preparation and measurement. For improving precision of measurement results, calibration, reference, and control standards as well as test sample solutions must be prepared as simultaneously as possible and freshly on each working day within the same work procedure, with the same equipment and under the same conditions. If larger numbers of reference and control standards are required for larger sample series, then the same dilution step for these standards must be repeated the required number of times whereby solutions can be collected in a single container. The temperatures of calibration, reference, and control standards as well as test sample solutions must be, to a large extent, the same during preparation and measurement. To achieve a constant aerosol production during nebulising, all configured solutions must, to a large extent, have the same acid concentration.
- Verification of accuracy of measurement results must be checked through independent control samples. The high-quality requirements on the control samples materials are safeguarded through use of synthetic or natural samples that demonstrate fertilizer-typical element composition and concentrations with their contents validated through reference procedures or validation in ring tests.
- Drift and background correction procedures (when required).
- Use of fertilizer type standardisation to increase the accuracy of the measurement (when required) by normalization of the sample value with ratio of the fertilizer type standard target value to measured value. This kind of type standardization can be used in addition to the daily instrument standardization to fine tune the calibration for known sample matrices. The element content of the final standard solutions for type standardisation should be at least as high as the element contents in the sample solutions to be tested. Element content nearing the limit of determination of the spectrometer may not be applied for type standardisation. Therefor the control samples can be used. Examples of fertilizer type standards for common fertilizer products are listed in 7.1.23 to 7.1.26.
- Undissolved fertilizer components (e.g. additives, conditioners) in the sample solutions can also have an influence on the aerosol production and are to be removed (filtered). When filtering the acidified sample test solution through paper filter, contamination can take place and lead to wrong results.
- The period to achieve the required plasma stability must be identified and established in preliminary tests. For different spectrometer types different running-in times in the range of 20 to 90 minutes were measured. Similarly, care should be taken that there is enough running-in time allowed for new pump hoses.
- Perform at least three replicates of each measurement and average the values if the values fall within the acceptance criterion of RSD ≤ 1% (short-term reproducibility).
- Monitoring of the long-term reproducibility (i.e. over a period of a month or a year) by using a applicable control sample with acceptance criteria of 3 % RSD for K_2O content of ≤ 15 % in the sample, 1,5 % RSD for (> 15 to ≤ 30) % K_2O, and 0,5 % RSD for > 30 % K_2O, respectively.
- The determined limit of quantification (LOQ) should reach at least 0,5 % K.

7.3.2 Interferences

7.3.2.1 General

Interferences and matrix effects shall be recognized and appropriate measures to minimize them shall be made. There are several types of interferences – see 7.3.2.2 to 7.3.2.6.

7.3.2.2 Spectral interferences

Spectral interferences are due to incomplete isolation of the radiation emitted by the analyte from other detected radiation sources. Spectral interferences are caused by the background emission from continuous or recombination phenomena, by stray light which causes background increase or overlap of a spectral line from another element, or by the unresolved overlap of molecular band spectra. Background emission and stray light can usually be compensated for by subtracting the background emission measured adjacent to the analyte wavelength peak. Background correction points on each side of the peak are used to correct a sloping background shift. The increase of background is more intensive with axial-view instruments. Background correction is not required in cases of line broadening where a background correction measurement would degrade the analytical result. A spectral line overlap usually leads to the choice of an alternative line. If this is not possible, mathematical correction procedures (e.g. inter-element correction technique or multi-component spectral fitting) can be used to compensate for the interference. These correction procedures are usually a part of the instrument software.

7.3.2.3 Transport interferences

Transport interferences are caused by differences in the properties between the sample solutions and the calibration solutions (viscosity, surface tension, density, dissolved solid content, type, and concentration of acids). Consequently, the supply of solution to the nebuliser, the efficiency of nebulisation and the droplet size distribution of the aerosol is altered, resulting in a change of sensitivity.

Errors due to these interferences can be overcome by dilution of the solutions, by matrix matching, by standard addition or by using an internal standard.

7.3.2.4 Excitation interferences

Excitation interferences are attributed to a change in the excitation conditions in the plasma, especially by the presence of easily ionisable elements. The interference depends on the operating conditions of the plasma (e.g. power, sample introduction, gas flowrate or observation height) and differ from element to element. Improvement of the plasma conditions can therefore reduce excitation interferences. Other possibilities are dilution of the solutions, matrix matching or the standard addition technique.

7.3.2.5 Chemical interferences

Chemical interferences are not significant with the ICP-OES technique, but if observed, they can be minimized by a careful selection of operating conditions (e.g. radio frequency power, observation position, gas flow rate and so forth).

7.3.2.6 Memory interferences

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. This type of interference may be caused by sample deposits or the accumulation in pump tubing, nebulizer, spray chamber, or plasma torch. The possibility of memory interferences should be recognized within an analytical run and suitable rinse steps and rinse times should be used.

7.3.3 Preparation of the test sample and blank solution

A blank test is prepared for the measurement following the same procedure as for samples.

In the final diluting step dilute the test sample solutions (5.3) by 1 + 24 (volume fraction) with the dilution solution (7.1.17) and mix well. Prepare a diluted blank solution by pipetting a blank solution and dilute in the same way as the test solution.

NOTE If an intermediate dilution is necessary, dilute an aliquot portion of the extract in one or more steps so that the final concentration of the element to be determined is in the middle of the given calibration range (7.3.4).

7.3.4 Preparation of the calibration standard solutions

The calibration standard solutions are prepared according to table 2. Add 250 ml water into a 500 ml graduated flask, transfer each respective volume listed in table 2, tempered, fill up to 500 ml with water and homogenise. The final concentrations of the calibration standard solutions are listed in table 3.

If necessary, calibration solutions of higher or lower concentrations may be prepared in the same way.

NOTE 1 For clarification, the purpose of combining calibration stock solution I & II is not only to act as a matrix modifier, but also to have almost the same salt concentration in each solution to increase the stability of nebulization and plasma during the ICP-OES measurement and therefore the reproducibility.

NOTE 2 To ensure the applicability to a wide range of inorganic fertilizers, it is necessary to carry out the initial calibration with all 14 calibration standard solutions. If you want to specialize this method on a specific fertilizer product, it is possible to reduce the number of calibration standards solutions to the desired working range (but use at least 5 standards).

NOTE 3 Alternatively, a Y-piece on the nebuliser can be used for on-line dosing of the internal standard (Li). In this case the Li standard stock solution (7.1.13) should not be added to the calibration standard solutions. To do so, the added Li solution concentration in the spray chamber (and plasma) should be chosen according to the intensity of the K signal. Also, it requires a very good, proven long-term precision of the on-line dosing method.

Table 2 – Preparation of the calibration standard solutions (end volume 500 ml)

Calibration standard solution #	Calibration stock solution I (7.1.15) in ml	Calibration stock solution II (7.1.16) in ml	Li standard stock solution (7.1.13) in ml	Nitric acid (7.1.2) in ml
1	20,0	0,0	2,5	5,0
2	19,8	0,2	2,5	5,0
3	18,0	2,0	2,5	5,0
4	16,2	3,8	2,5	5,0
5	14,6	5,6	2,5	5,0
6	12,8	7,2	2,5	5,0
7	11,0	9,0	2,5	5,0
8	9,0	11,0	2,5	5,0
9	7,2	12,8	2,5	5,0
10	5,6	14,6	2,5	5,0
11	3,8	16,2	2,5	5,0
12	2,0	18,0	2,5	5,0
13	0,2	19,8	2,5	5,0
14	0,0	20,0	2,5	5,0

Table 3 – Concentrations of potassium and K_2O of the calibration standard solutions in mg/l and as mass fraction in % (based on a sample weight of 10 g in 1 000 ml and further dilution of 1 + 24 volume fraction), respectively.

Calibration standard solution #	Potassium concentration		K_2O concentration	
	in mg/l	in %	in mg/l	in %
1	0,00	0,00	0,00	0,00
2	2,09	0,52	2,52	0,63
3	20,88	5,22	25,15	6,29
4	39,67	9,92	47,79	11,95
5	58,46	14,62	70,42	17,61
6	75,17	18,79	90,55	22,63
7	93,96	23,49	113,18	28,30
8	114,84	28,71	138,34	34,58
9	133,63	33,41	160,97	40,25
10	152,42	38,10	183,61	45,90
11	169,12	42,28	203,72	50,93
12	187,91	46,98	226,36	56,59
13	206,71	51,68	249,00	62,25
14	208,79	52,20	251,51	62,88

7.3.5 Measurement

7.3.5.1 Instrument conditions

Due to differences between various kinds of instruments, no detailed instructions can be given to operate the specific instrument. The instruction provided by the manufacturer for waiting time, instrument stability, gas flows, plasma conditions, nebuliser conditions, sample uptake rate, rinse time, measuring time etc. should be followed.

Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects will be investigated and established for each individual analyte line on that particular instrument. The aim is to find the best sensitivity and precision and to minimize interferences for the set of lines to be used. It is recommended to use the analyte lines at wavelengths 766,491 nm for K and 670,780 nm for Li. Emission efficiency is related, amongst other parameters, to the plasma temperature, which is a function of RF power, argon gas flows and observation height (for radially viewed plasmas). Also, the type of nebuliser and sample uptake rate will have an impact on the signal and the background.

Set up the instrument with the proper operating parameters established from the manufacturer's instruction manual and preliminary tests. Allow the instrument to achieve thermal stability before beginning. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the calibration standard solutions (7.3.4). The relationship between concentration and intensity is linear up to six orders of magnitude for the most ICP-OES instruments.

All test solutions, blanks and calibration solutions are measured under the same optimized conditions using background correction and other suitable steps to eliminate or minimize interferences.

7.3.5.2 Measurement programme

In the instrument software the measurement sequence is established as follows:

1. Calibration standard solutions (7.3.4)

2. Fertilizer type standard solution, depending on fertilizer type (7.1.23 to 7.1.26)

3. Test and blank sample solutions (max. 10)

4. Control samples, depending on fertilizer types (7.1.18 to 7.1.22)

5. Fertilizer type standard solution, depending on fertilizer type (7.1.23 to 7.1.26)

For further analysis solutions the steps 3 to 5 are repeated.

The (re)calibration takes place using at least two standards that together cover the entire work area, e.g. 2nd and 14th calibration standard solution (7.3.4).

If necessary, a drift correction and/or fertilizer type standardisation can be calculated via the fertilizer type standard solution (7.1.23 to 7.1.26). Several analysis solutions can be measured between two fertilizer type standard solutions. Their number is to be selected in such a way that, through the applied control sample, signal drift of the measurement system can be identified and corrected per calculation with sufficient reliability.

The configured (re)calibration solutions and analysis solutions are entered into the sample list of the equipment software and the measurement is started.

Ensure that the concentration values of the control samples do not deviate from the target values by more than the established tolerance limits (see 7.1.18 to 7.1.22). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

Whenever an unknown matrix is encountered, check the following:

— Matrix effects by running a spiked sample.

— Matrix effects by analysing at a different wavelength, i.e. 769,90 nm.

7.4 Calculation and expression of the results

The software of the instrument or an external software is used to calculate concentrations of the elements in the individual test solutions, incl. drift correction and fertilizer type standardisation.

The result can be directly evaluated from the calibration function and is expressed as mass fraction of K_2O, expressed as per cent of the fertilizer (w_{K2O})

8 Precision of method A and B

This subclause is going to be included after conduction inter-laboratory ring tests.

8.1 Inter-laboratory tests

8.2 Repeatability

8.3 Reproducibility

9 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample.
b) the test method used with reference to this document, prEN 00260271:2024.
c) the test results obtained.
d) date of sampling and sampling procedure (if known).
e) date when the analysis was finished.
f) whether the requirement of the repeatability limit has been fulfilled.
g) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

Bibliography

[1] *Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003*

[2] EN 1482-1, *Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling*

[3] EN 1482-3, *Fertilizers and liming materials — Sampling and sample preparation — Part 3: Sampling of static heaps*)

[4] EN 15477, *Fertilizers — Determination of the water-soluble potassium content*

[5] EN 16963, *Fertilizers — Determination of boron, cobalt, copper, iron, manganese, molybdenum, and zinc using ICP-AES*

[6] EN ISO 7407, *Fertilizers — Determination of acid-soluble potassium content — Preparation of the test solution*

[7] EN ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

[8] VDLUFA II.1, 4.2.4 (2014) — *Determination of Ca, K, Mg, Na, P, S and Cl as macro and secondary nutrients in fertilisers*