

Application Bulletin 134/2e

Determination of potassium with an ion-selective electrode

Branch

General analytical chemistry; food, stimulants, beverages; fertilizers, base materials, explosives; water, wastewater, environmental protection

Keywords

Potassium; ISE; ion-selective electrode; standard addition; direct measurement; branch 1; branch 2, branch 7; branch 11; 6.0510.110; soil; fertilizer; juice; wine; water; electrolyte powder

Summary

Potassium is one of the most common elements and can be found in many different minerals and other potassium compounds. It is of importance for humans, animals and plants as it is an essential mineral nutrient and involved in many cellular functions like cell metabolism and cell growth.

For these reasons, it is important to be able to declare the potassium content of food or soil to reduce problems that may arise by a potassium deficiency or extensive consumption. Often, potassium is determined by flame photometric method. However, flame photometry is only linear over a limited concentration range and often sample dilution is necessary. Furthermore, the instrumentation is rather complex and expensive to purchase and maintain.

This bulletin describes an alternative to flame photometric method using an ion selective electrode and direct measurement or standard addition technique. Several potassium determinations in different matrices using the combined potassium ion-selective electrode (ISE) are presented here. Additionally, general hints, tips and tricks for best measurement practice are given.

Instruments

- Ion Meter or Titrator with the modes MEAS CONC and/or STDADD
- Stirrer
- Buret 10 mL (Standard addition)

Electrodes

Combined polymer membrane ISE, K	6.0510.110
Temperature sensor Pt1000	6.1110.100

General hints

Handling of the electrode

To achieve optimal measurements, the following points are essential:

- The ion sensing part of the potassium electrode is made of a polymer membrane containing an ion specific ionophor. Any deposition of fat or scratching the membrane should be avoided, therefore it should neither be touched with your bare hands nor cleaned with abrasives.
- The lifetime of a polymer membrane electrode is limited. The mean lifetime at normal lab use is about half a year, however the lifetime strongly depends on the application type and how the electrode is maintained.
- The potassium ISE must be stored dry with some residual moisture (e.g., some drops of deionized water) in the electrode vessel to keep the reference system ready.
- For a short period of time the electrode can be stored in $c(\text{KCl}) = 0.01 \text{ mol/L}$. Storage in reference electrolyte is not recommended as the electrolyte does not contain K ions and therefore will leach out the ionophor.
- When the electrode was not in use for a longer period of time, conditioning of the polymer membrane in $c(\text{KCl}) = 0.01 \text{ mol/L}$ for 30 min is recommended to shorten the response time.
- The electrode should only be used in aqueous solutions as otherwise the polymer membrane is affected (softeners are leached out, resulting in a hard membrane that does not respond properly anymore).
- Rinse the electrode after each measurement with deionized water.
- When conducting a series of measurements and an increase of the measured content is visible under otherwise identical conditions, the electrode should be conditioned for 5 min in $c(\text{KCl}) = 0.01 \text{ mol/L}$.

- The K-ISE has a high cross sensitivity for ammonium ions. Therefore, it is important to remove those prior to analysis from the sample matrix.
- The pH of the sample has to be adjusted to 2.5 to 11. If the solution is too acidic, H⁺ ions may interfere.
- To check the performance of the K-ISE, the potential of two solutions, first c(KCl) = 10⁻⁴ mol/L and second c(KCl) = 10⁻³ mol/L is measured. The potential difference between the two measurements should be higher than 47.3 mV (at 25 °C).

Choice of procedure

The choice of the procedure depends on the sample matrix, the number of samples to analyze and the concentration range of K in the sample.

- For measuring samples with a complex or unknown matrix, it is the best to use the standard addition. A direct measurement is recommended with an unproblematic sample matrix.
- For large sample numbers or online measurements, direct measurement is recommended.
- In case of low-level measurements, it is recommended to either use direct measurement after calibration or spike the sample to a higher K content. The reason for this is that otherwise the sensor is at the limit of detection and outside its linear range, which leads to too high results for standard addition.

Sample preparation and parameters

The sample preparation and the parameters are mentioned in the section *Practical examples*.

Direct measurement

Direct measurement is recommended for unproblematic samples and in case of low-level measurements (mg/L or µg/L range).

In case of a direct measurement, the following points have to be considered:

- The standard solutions used for calibration must have the same ionic background as the sample solutions. Therefore, the identical amount of ISA should be added to all calibration standards and all sample solutions.
- For calibration standards and samples with concentrations < 1 mg/L, diluted ISA should be used as otherwise the response time of the sensor becomes distinctly longer.

- All measurements should be performed at a constant temperature (for example 25 °C) as the slope of the ISE is temperature dependent (Nernst).
- For more accurate results, the use of a temperature sensor or a thermostated titration vessel is recommended.
- Perform the calibration and the measurements at identical stirring conditions.

Standard addition

Standard addition is recommended for undefined or complex sample matrices.

There are three types of standard addition:

- manual
- auto dos
- auto

The quickest and recommended method is automatic standard addition (mode: «auto»). In order to get exact results the potential difference ΔU should be at least 12 mV per standard addition and at least 3 standard additions should be performed (total ΔU of at least 36 mV). If exactly defined volumes of the standard additions are required but maximum ease of operation is also desirable, the mode «auto dos» is recommended. In this case the individual standard addition volumes can be defined (see manual of the device in use or the help of the software).

The volume of the added solution / the concentration of the standard must be chosen in such a way that the dosed volume does not exceed 25% of the sample volume and the buret must not be refilled during addition.

The calculation of the result is automatically carried out by the instrument applying an iteration procedure.

In case of standard addition, the following points have to be considered:

- Stirring is necessary during additions. Additions without continuous stirring lead to false results.
- If the total volume added during standard addition is higher than 25 % of the initial solution, the sample has to be diluted prior to the analysis with ISA or deionized water or a standard of higher concentration has to be used for the addition.
- In order to ensure an accurate evaluation of the standard addition, the standard concentrations (C_{std}) for the different buret volumes (V_{buret}/mL) must be chosen as a function of the sample concentration (C_{smpl})

according to the table below. Thereby any sample dilution has to be considered (e.g., dilution with ISA)

Table 1: Ratio of the standard concentration and sample concentration in dependency of the buret volume

V_{buret} in mL	$C_{\text{std}} : C_{\text{smpl}}$
5	40 : 1
10	20 : 1
20	10 : 1
50	5 : 1

Example factor determination

Sample concentration (C_{smpl}):	5 mg/L
Buret volume (V_{buret}):	10 mL
Sample size:	10 mL
ISA volume:	10 mL
Total volume (V_{total}):	20 mL
Factor from table 1 ($C_{\text{std}} : C_{\text{smpl}}$):	20

Considering the dilution with ISA the initial sample concentration is 2.5 mg/L. The optimal concentration of the standard is therefore:
 $2.5 \text{ mg/L} \cdot 20 = 50 \text{ mg/L}$.

Comments

- Potassium can also be determined by titration with sodiumtetraphenylborate (STPB).

Practical examples

Reagents

The following reagents are needed to prepare the potassium standard and ISA (Ionic Strength Adjuster).

- Potassium chloride
- Sodium chloride

For sample preparation, various other reagents like acids, bases or extraction solutions might be necessary. They are specified in the respective chapters.

Solutions

Potassium standard	$\beta(\text{K}^+) = 10'000 \text{ mg/L}$ 18.64 g of dried potassium chloride is weighed into a 1 L volumetric flask and filled up to the mark with deionized water. Other concentrations are prepared the same way by adjusting the amount of dried potassium chloride.
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ISA	$c(\text{NaCl}) = 3 \text{ mol/L}$ 175.3 g sodium chloride is weighed into a 1 L volumetric flask and filled up to the mark with deionized water.
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Potassium in water samples by direct measurement

Sample

- Surface water

Solutions

- Potassium standard $\beta(K^+) = 120 \text{ mg/L}$
- ISA $c(\text{NaCl}) = 3 \text{ mol/L}$

Sample preparation

No sample preparation is required.

Standard preparation

Standard	1	2	3	4
Concentration / (mg/L)	1.2	2.4	4.8	9.6

The calibration standards are prepared by diluting the potassium standard $\beta(K^+) = 120 \text{ mg/L}$ to the desired concentrations.

Analysis

Calibration

Just before measurement 0.5, 1, 2 or 4 mL of $\beta(K^+) = 120 \text{ mg/L}$ is dosed into the calibration beaker, 2 mL ISA is added and the beaker is filled to 50 mL with deionized water. The measurement of the respective calibration standard is carried out. In between the measurements of the calibration standards, the electrode is well rinsed with deionized water.

Sample

1.6 mL ISA is added to 40 mL sample and the direct measurement is carried out. In between each measurement the electrode is conditioned for 30 s in $c(\text{KCl}) = 0.01 \text{ mol/L}$ and then well rinsed with deionized water.

Parameters

Mode	CAL Conc	MEAS Conc
Signal drift	0.2 mV/min	0.2 mV/min
Min. waiting time	10 s	10 s
Max. waiting time	300 s	300 s
Measuring interval	2.0 s	2.0 s
Stirring rate	8	8

Results

Calibration

Measured values

Standard	Conc. / (mg/L)	U / mV
1	1.2	-280.0
2	2.4	-265.4
3	4.8	-249.7
4	9.6	-233.8

Slope: 54.8 mV
 E(0): -287.6 mV
 c(blank): 0.20 mg/L
 Variance: 0.020

Sample

Sample	Concentration / (mg/L), n = 3
Surface water	2.346 ($S_{\text{rel}} = 0.24\%$)

Example determination

Calibration

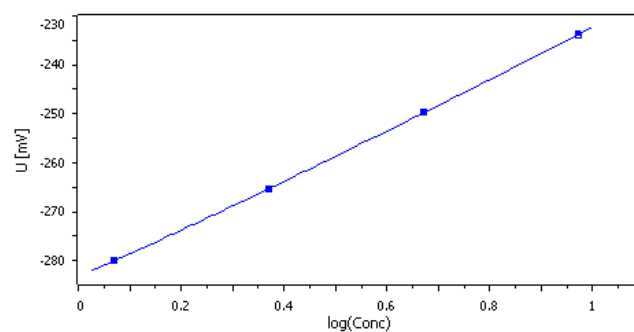


Fig. 1: Calibration curve

Sample

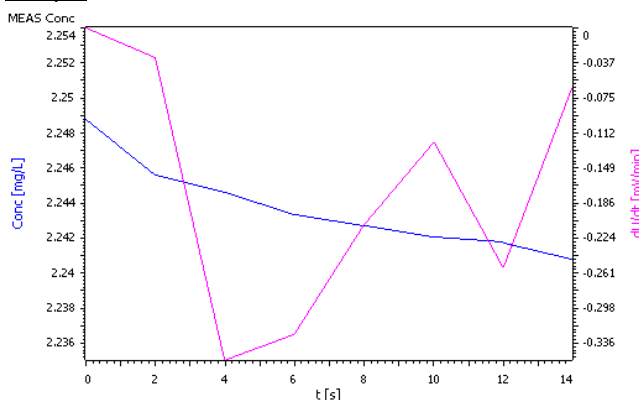


Fig. 2: Measurement of K in surface water sample.

Potassium in fruit juices and wine with automatic standard addition

Samples

- Orange juice
- Apple juice
- Wine

Solutions

- Potassium standard $\beta(K^+) = 4000$ mg/L
- ISA $c(NaCl) = 3$ mol/L

Sample preparation

No sample preparation is required.

Analysis

1 mL sample and 2 mL ISA are pipetted into the titration vessel and diluted with 47 mL deionized water. The standard addition is carried out with $\beta(K^+) = 4000$ mg/L. In between each measurement the electrode is conditioned for 30 s in $c(KCl) = 0.01$ mol/L and then well rinsed with deionized water.

Parameters

Mode	STDADD auto
Number of additions	4
Volume auxiliary solution	49 mL
Stop volume	10 mL
Dosing rate	Medium
Delta U	15 mV
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	300 s
Measuring interval	2.0 s
Stirring rate	8
Mode	STDADD auto

Calculation

The calculation of the result is automatically carried out by the instrument applying an iteration procedure.

Results

Increment	dV / mL	U / mV	dU / mV
0	/	-274.7	/
1	0.264	-259.1	15.6
2	0.479	-243.8	15.3
3	0.893	-228.7	15.1
4	1.710	-213.6	15.0

Slope: 58.0 mV
 E(0): -354.8 mV
 K(+1): 1207.2 mg/L
 Variance: 0.002

Sample	Result in mg per 100 mL, n = 5
Apple juice	121.4 ($s_{rel} = 0.6\%$)
Orange juice	203.9 ($s_{rel} = 1.0\%$)
Red wine	124.9 ($s_{rel} = 0.6\%$)

Example determination

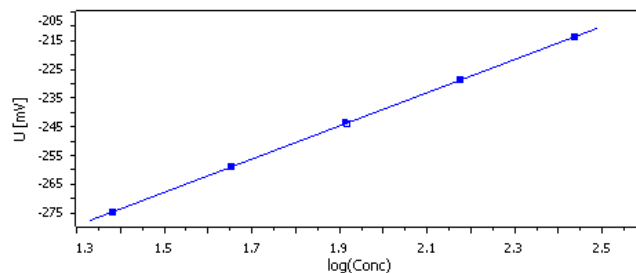


Fig. 3: Curve of the standard addition for apple juice.

Potassium in electrolyte powder with automatic standard addition

Sample

- Electrolyte powder

Solutions

- Potassium standard $\beta(K^+) = 10'000 \text{ mg/L}$
- ISA $c(\text{NaCl}) = 3 \text{ mol/L}$
- $c(\text{NaOH}) = 1 \text{ mol/L}$

Sample preparation

The electrolyte powder is dissolved in 250 mL deionized water.

Analysis

5 mL sample, 1 mL $c(\text{NaOH}) = 1 \text{ mol/L}$ and 10 mL ISA are pipetted into the measurement vessel and diluted with 34 mL deionized water. The standard addition is carried out with $\beta(K^+) = 10'000 \text{ mg/L}$. In between each measurement the electrode is conditioned for 30 s in $c(\text{KCl}) = 0.01 \text{ mol/L}$ and then well rinsed with deionized water.

Parameters

Mode	STDADD auto
Number of additions	4
Volume auxiliary solution	45 mL
Stop volume	10 mL
Dosing rate	Medium
Delta U	15 mV
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	300 s
Measuring interval	2.0 s
Stirring rate	8

Calculation

The calculation of the result is automatically carried out by the instrument applying an iteration procedure. The obtained result has to be multiplied by the dilution factor to get the K^+ content per serving.

Results

Increment	dV / mL	U / mV	dU / mV
0	/	-214.3	/
1	0.368	-199.1	15.2
2	0.678	-184.0	15.1
3	1.293	-168.9	15.0
4	2.558	-154.0	14.9

Slope: 57.0 mV
 E(0): -324.1 mV
 K(+1): 845.6 mg/L
 Variance: 0.004

Sample	Result in mg per serving, n = 5
Electrolyte powder	56.9 ($s_{\text{rel}} = 0.5\%$)

Example determination

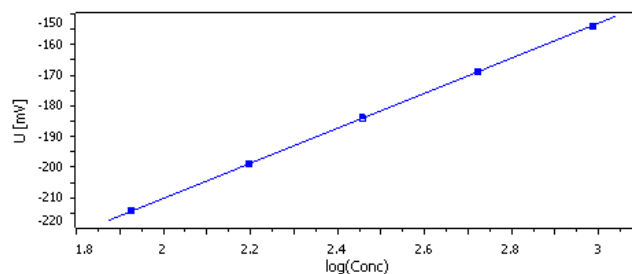


Fig. 4: Curve of the standard addition for electrolyte powder.

Potassium in fertilizer with automatic standard addition

Sample

- Liquid fertilizer
- Solid fertilizer

Solutions

- Potassium standard $\beta(K^+) = 10'000 \text{ mg/L}$
- ISA $c(\text{NaCl}) = 3 \text{ mol/L}$
- $c(\text{NaOH}) = 2 \text{ mol/L}$

Sample preparation

Approx. 5 g of liquid fertilizer or 2.5 g of homogenized solid fertilizer is weighed accurately into a 50 mL volumetric flask and filled up to the mark with $c(\text{NaOH}) = 2 \text{ mol/L}$. The solution is vigorously shaken and allowed to stand for about 1 hour to release all ammonia.

Analysis

0.5 (solid fertilizer) or 1 mL (liquid fertilizer) of the prepared sample solution and 10 mL ISA are pipetted into the measurement vessel and diluted with deionized water to 50 mL. The standard addition is carried out with $\beta(K^+) = 10'000 \text{ mg/L}$. In between each measurement the electrode is conditioned for 30 s in $c(\text{KCl}) = 0.1 \text{ mol/L}$ and then well rinsed with deionized water.

Parameters

Mode	STDADD auto
Number of additions	4
Volume auxiliary solution	49.5 (solid fertilizer) or 49 mL (liquid fertilizer)
Stop volume	10 mL
Dosing rate	Medium
Delta U	12 mV
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	300 s
Measuring interval	2.0 s
Stirring rate	8

Calculation

The calculation of the result in mg/L is automatically carried out by the instrument applying iterative procedure. To obtain

the mass fraction of potassium oxide declared for fertilizer, an additional calculation has to be performed:

$$w_{K_2O} = \text{Res}_{\text{stdadd}} \times \frac{M_{K_2O} \times V_{\text{sample}}}{2 \times M_K \times m_{\text{sample}}} \times 100$$

w_{K_2O}	Mass fraction of potassium oxide in % (w/w)
$\text{Res}_{\text{stdadd}}$	Result given from standard addition in mg/L
M_{K_2O}	Molar mass of potassium oxide in g/mol
2	Stoichiometric factor
M_K	Molar mass of potassium in g/mol
V_{sample}	Final dilution volume in L, here 0.05 L
m_{sample}	Sample size of fertilizer in g
100	Factor for %

Results

Increment	dV / mL	U / mV	dU / mV
0	/	-191.8	/
1	0.204	-179.5	12.3
2	0.342	-167.3	12.3
3	0.573	-155.2	12.1
4	0.980	-143.1	12.0

Slope:	54.9 mV
E(0):	-289.3 mV
K(+1):	5954.9 mg/L
Variance:	0.001

Sample	$\omega(K_2O)$ in % (m/m), n = 5
Liquid fertilizer	10.46 ($S_{\text{rel}} = 0.71\%$)
Solid fertilizer	10.04 ($S_{\text{rel}} = 1.19\%$)

Example determination

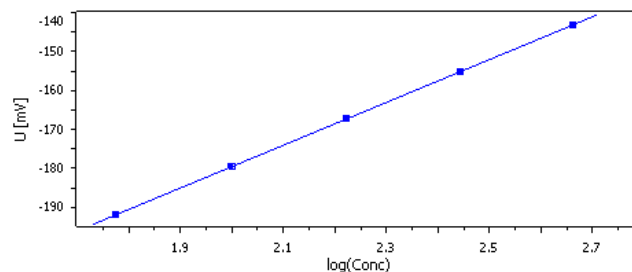


Fig. 5: Curve of the standard addition for a solid fertilizer sample.

Potassium in soil with automatic standard addition

Sample

- Flower soil

Solutions

- Potassium standard $\beta(K^+) = 4000$ mg/L
- ISA $c(NaCl) = 3$ mol/L
- CAL test solution, stock solution diluted 1:5

CAL stock solution	7.7 g calcium lactate and 3.95 g calcium acetate are dissolved in approx. 50 mL deionized water. 5 mL glacial acetic acid is added and afterwards the pH is adjusted to 4.1 by adding dropwise glacial acetic acid. The solution is transferred into a 100 mL volumetric flask and filled up to the mark with deionized water.
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Sample preparation

Approx. 5 g dried soil (2 h at 120 °C), a spatula of active carbon and 100 mL of CAL test solution are added into a glass beaker. The mixture is stirred at high stirring rate for 2 hours and afterwards the suspension is filtrated.

Analysis

5 mL of extracted and filtered sample is pipetted into a 120 mL beaker, 2 mL of ISA is added and then the solution is diluted with deionized water to 50 mL. The standard addition is carried out with $\beta(K^+) = 4000$ mg/L. In between each measurement the electrode is conditioned for 30 s in $c(KCl) = 0.01$ mol/L and then well rinsed with deionized water.

Parameters

Mode	STDADD auto
Number of additions	4
Volume auxiliary solution	45 mL
Stop volume	10 mL
Dosing rate	Medium
Delta U	12 mV
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	300 s

Stirring rate	8
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Calculation

The calculation of the result is automatically carried out by the instrument applying iterative procedure.

Results

Increment	dV / mL	U / mV	dU / mV
0	/	-206.6	/
1	0.261	-194.1	12.5
2	0.431	-182.0	12.1
3	0.732	-169.9	12.1
4	1.263	-157.8	12.1

Slope: 54.8 mV
 E(0): -287.5 mV
 K(+1): 299.4 mg/L
 Variance: 0.000

Sample	$\omega(K^+)$ in % (m/m), n = 5
Flower soil	1.181 ($S_{rel} = 1.10$)

Example determination

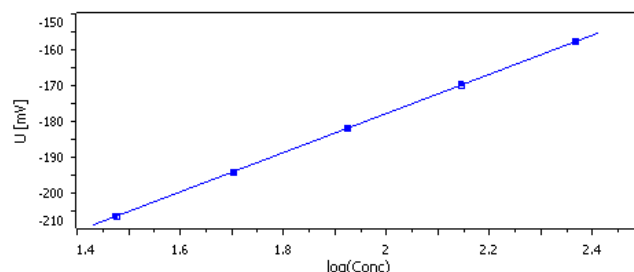


Fig. 6: Standard addition of the CAL soil extract.

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