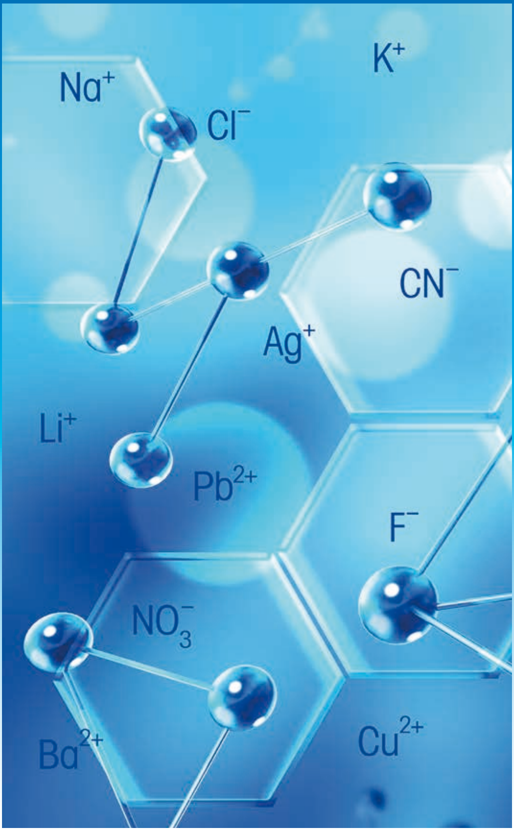
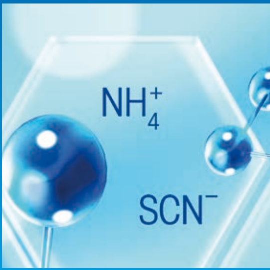
ISE Theory Guide





Applications
Practical Hints
Theory

ISE
Measurements
in the Laboratory

A Guide for Ion-Selective Electrodes

Theory and Practice of ISE Applications

METTLER TOLEDO

Preface

Ion-selective electrodes (ISEs) have been developed for practical use in the 1960s by several research groups and sensor manufacturers. Since then, ISEs have become well-established tools, providing a fast and simple method to measure ion activity. However, research and development have continued revealing new applications of this potentiometric analysis technique.

Another appreciated benefit of ISE methods is the favorable investment cost. The purchase of a complete measuring system (ion electrode and ion meter) is comparable to the purchase of the ubiquitous pH measurement system.

Nowadays, ISE users have access to a series of reliable sensors, suitable ion meters and helpful accessories. A large number of applications has been drawn up to master the ion concentration determination in many samples. Samples originate from a variety of sources such as food, beverage, water, environment, medicine, pharmaceuticals and chemicals.

Reliable ion-selective electrodes and modern meter instruments provide easy operating procedures, safe user guidance, as well as impeccable data handling and storage. Automation of ion-selective measurement workflows by hardware components and software solutions further contributes to safe and efficient laboratory work.

Disclaimer

This guide presents general information and selected application examples. The information is based on the current state of our knowledge.

The application experiments were conducted with the utmost care using the instruments specified in the description of each application. The results were evaluated according to the current state of our knowledge. This does not however absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility.

When chemicals, solvents and gases are used, general safety rules and the instructions given by the manufacturer or supplier must be observed.

Content

1. What ISEs Can Do

Ion-selective electrodes (ISEs) are a modern analytical tool for fast and direct ion activity determination of sample solutions. Together with a suitable ion meter or titrator, ISEs form a well affordable and versatile measuring system. The theory behind ISEs relies on the Nernst equation, just as the pH theory does. Hence, ISE techniques are easily understood and in many cases simply applied.

1.1 When to use ion-selective electrodes

Ion-selective electrodes are used to determine the activity of the ion under consideration (analyte ion). The ion has to be dissolved preferably in water. When the sample does not dissolve, other methods need to be implemented first, in order to bring the ion into solution. Normally color and turbidity of a sample do not disturb the measurement. Alternative analytical techniques for measuring ion activity are ion chromatography (IC) and titration. For IC, the sample solution has to be clear, the analyte ion concentration lies preferably in the ppm range and the equipment costs are higher than for ISEs.

ISEs work under conventional laboratory conditions. The typical measuring range extends from 10^{-1} to 10^{-6} mol/L. The temperature ranges from 0 °C to 50 or 80 °C, depending on the type of ISE. However, the prevailing values are 20, 25 and 37 °C. The admissible pH range is moderate and excludes highly alkaline or extremely acidic samples.

These generous conditions allow ISE methods to be used in a wide spectrum of applications. Chemical and pharmaceutical samples as well as environmental monitoring, water quality tests, food, and plants are well suited for ISE analysis. ISEs are particularly applicable to biological and medical samples because they measure ion activity.

ISEs for cations	**ISEs for anions**
Ammonium, barium, calcium, cadmium, copper, lead, lithium, potassium, silver, sodium	Bromide, chloride, cyanide, fluoride, fluoroborate, iodide, nitrate, sulfide, thiocyanate

1.2 How ion-selective electrodes work

Ion-selective electrodes come either as combined electrodes or as half cells. In the first ones, the measuring and the reference electrodes are combined in one sensor. A half-cell comprises the ion-selective element only. To achieve a complete sensor system, a suitable reference electrode has to be added.
The sensing element of the ISE is the ion-selective membrane, which produces different potentials at different ion concentrations. Hence, the potential difference between the ion-selective and the reference electrode varies accordingly and is measured with an ion meter. Find details about the membranes in chapter 1.4.

This potential difference is proportional to the activity of the selected ion in solution. The activity of an ion is modulated by its concentration and the ionic strength of the sample solution. In the daily practice, instead of activity the ion concentration is evaluated (see box). The usual concentration units are mol/L, mg/L or ppm.
The relation between the ion activity and the measured potential difference, also called electrode potential, is described by the **Nernst** equation:

$$E = E_o + 2.3\ (R\ T / n\ F) \bullet \log a_i$$

E measured electrode potential, mV
E_o standard potential (a constant for a given electrode), mV
R gas constant, J/mol K
T temperature, K (standard temperature 25 °C (298.15 K))
n ionic charge (the symbol z is also used)
F Faraday constant, C/mol
a_i activity of analyte ion i
c_i concentration of analyte ion i

Activity vs Concentration

ISEs respond to the activity of the analyte ion a_i. However, ion concentration c_i is used in the laboratory for practical reasons.

$a_i = f \bullet c_i$

For ion concentrations ≤1 mol/L, i.e. in diluted samples, the factor f becomes 1. Hence, the Nernst equation then is

$E = E_o + 2.3\ (R\ T / n\ F) \bullet \log c_i$

The term (R T / n F) is the Nernst factor, also called slope factor or simply slope. The slope value calculated from this term is called ideal slope or 100% slope. It has the unit volt or millivolt. Because n is part of the formula, the slope depends on the ionic charge of the ion considered.

Ionic charge	+2	+1	–1	–2
Ideal slope	29.58	59.16	–59.16	–29.58
Example ions	Ca^{2+}, Cu^{2+}	K^+, Ag^+	F^-, NO_3^-	S^{2-}

Table 1.1: Ionic charge and slope at room temperature. Unit of the slope: mV.

The slope also depends on the temperature according to the formula. It increases with increasing temperature.

Temperature	20 °C	25 °C	30 °C	37 °C	40 °C
Slope (n = +1)	58.17	59.16	60.15	61.54	62.14

Table 1.2: Influence of the temperature on the slope of an electrode.
Unit of the slope: mV.

1.3 Selectivity

Ion-selective electrodes are sensitive to the analyte ion activity (see chapter 1.2). However, they are also sensitive to other ions to a certain extent. This influence of interfering ions is expressed as the selectivity coefficient. It defines the preference of the ISE for the analyte ion, compared to the interfering ion. Selectivity coefficients are empirical values valid for the respective ISE and the interfering ions stated.

Selectivity Coefficient K

Example:

$K(K^+ / Na^+) = 2.6 \cdot 10^{-3}$

The preference for K^+ over Na^+ for this potassium ISE is 1 to $2.6 \cdot 10^{-3}$ or 385 to 1. This means that the potassium ISE is 385 times more selective to K^+ than to Na^+.

Nicolsky has extended the Nernst equation to include the contributions of interfering ions to the measured potential E of an ISE:

$$E = E_o + 2.3\ (R\ T / n_i\ F) \bullet \log\ [a_i + \sum_{j \neq i} (K_{ij} \bullet a_j^{\,n_i/n_j})]$$

$\sum\limits_{j \neq i}$	sum of all K_{ij} for all interfering ions j
K_{ij}	selectivity coefficient for analyte ion i over interfering ion j
a_j	activity of interfering ion j
n_i	ionic charge of analyte ion i
n_j	ionic charge of interfering ion j

1.4 Types of ion-selective electrodes

The most relevant part of an ion-selective electrode is the ion-selective membrane. The composition of the membrane depends on the analyte ion. For routine use, there are three different membrane types. The basic structure of an ion-selective electrode is comparable to a pH electrode, which is familiar to most people working in a laboratory. The schematic design of a combined ISE is depicted in Figure 1.1

Crystalline membrane (solid state membrane)	The potential difference is measured across a solid mono- or polycrystalline membrane. As an example, a monocrystalline lanthanum fluoride LaF_3 membrane is used for the fluoride ISE. Crystalline membranes are robust and provide a long lifetime.
Polymer membrane (liquid membrane)	The selective compound (ionophore) is embedded in a polymer membrane, usually PVC. Initially, liquid ion exchangers were used. Later, other organic compounds have been found more suitable e.g. antibiotics or crown ethers. Further ingredients such as plasticizers enhance the performance of the ISE. Polymer membranes are delicate. Hence, avert mechanical distortions. They are also sensitive to organic solvents due to swelling of the membrane and elution of the ingredients.
Glass membrane	The most common glass membrane ISE is the pH electrode measuring H^+ ions. Another example is the sodium ISE from METTLER TOLEDO with its membrane glass sensitive for Na^+. A major advantage of glass membrane electrodes is their chemical resistance.

Table 1.3: Membrane types of ISEs.

Polymer and crystalline membranes are often manufactured as replaceable sensing modules. This helps to save the entire electrode body when the sensing membrane has come to the end of operation or in case of mechanical defects or chemical deterioration. It is also easy to disassemble such an electrode for long term (dry) storage. For storage conditions see chapter 4.6.

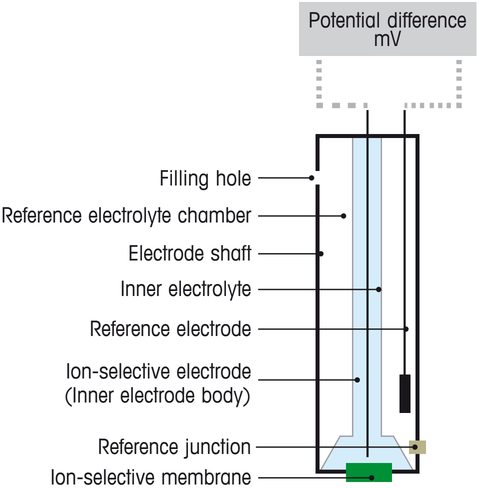


Figure 1.1: Illustration of a combined ISE.

1.5 Typical measuring range

The measuring range of an ISE typically covers 5 to 6 decades of concentration. The range starts usually at 10^{-1} mol/L. At concentrations of around 10^{-6} mol/L the limit of quantitation (LoQ) is reached. Hence, the range corresponds approximately to 0.1 to 1000 ppm.

For low-level measurements, i.e. in the non-linear region, special measurement procedures are applied. See chapter 1.10 and the ISE instructions for more details.

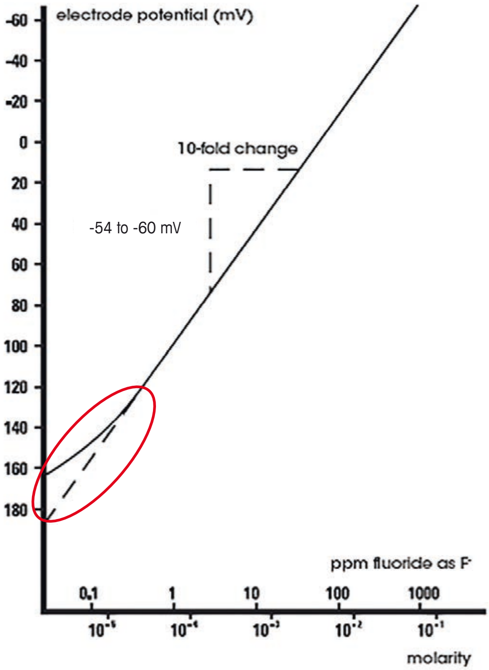


Figure 1.2: Calibration curve of a Fluoride ISE. The electrode response behavior is non-linear in the marked area.

1.6 Electrode response

The response time of an electrode (i.e. the time required to reach 99% of a stable potential reading) varies from a few minutes in concentrated solutions to several minutes near the limit of detection. In general, crystalline and glass membrane electrodes manifest shorter response times than polymer membrane ISEs. A very slow response indicates the end of the ISE operating period: the membrane module or electrode must be replaced. For more details about electrode response, see the ISE instructions.

Typical response times of new and well-conditioned ISEs:
- Crystalline and glass membranes: 3 to 5 minutes
- Polymer membranes: 5 to 8 minutes

Appropriate stirring and an increased outflow of reference electrolyte usually help shorten the response time.

Figure 1.3: A selection of ISEs.

1.7 Limitations

Applications of ISEs are mainly limited by the sample matrix, i.e. interfering ions and ionic strength. For many applications and samples, the influence of interfering ions is not relevant and can be ignored.

The sum of all influences from all the ions present in the sample is called ionic strength. As the Nicolsky equation shows (chapter 1.3), ionic strength is a function of the molar concentration (activity) of ions and their ionic charge. The addition of ionic strength adjustment (ISA) solutions helps to maintain a constant ionic strength and control the influence of varying ionic compositions.

ISE	**Interfering ions** (decreasing order of interference)
Fluoride	OH^-
Chloride	Hg^{2+} must be absent. CN^-, I^-, S^{2-}, Br^-, NH_3, OH^-
Calcium	Pb^{2+}, H^+, Fe^{2+}, Cu^{2+}, Na^+, K^+, Ba^{2+}, Zn^{2+}, Mg^{2+}
Potassium	Cs^+, NH_4^+, H^+, Li^+, Na^+

Table 1.4: Typical interfering ions of some frequently used ISEs.

Interference countermeasures

ISA solutions aim to maintain a constant ionic strength and control the influence of varying ionic compositions. Therefore, ISA solutions have to be added equally to samples and standard solutions to achieve a uniform ionic strength. For ISA solutions see chapter 3.3. Adequate sample preparation, incremental techniques, and adapting the standard solutions are further options to reduce the influence of interfering ions. Also, the addition of reagents can contribute to diminish interferences.
The supplemental adjustment of the pH value with a suitable pH buffer is only required if the pH value lies outside the admissible pH range.

Example 1: adjust the pH value of the sample to 4 or 4.5 with sulfuric or nitric acid to avoid the influence of OH^-, HCO_3^- and CO_3^{2-} ions.

Example 2: precipitate halides and cyanide with silver ions by adding e.g. silver sulfate (Ag_2SO_4).

Example 3: add nickel ions (Ni^{2+}) to remove interfering sulfide and cyanide ions.

Refer to the ISE operating instructions for information on interfering ions, interfering concentrations and recommended countermeasures.

1.8 Measurement procedures

The measurements with ISEs follow two main procedures: direct determination or incremental methods.

Direct determination

With direct potentiometry, the sample concentration is determined from a calibration curve, assuming that the electrode's response is the same for sample and standard solutions. The calibration curve can be drawn with the measured values obtained from a mV/pH or ion meter. However, direct potentiometry using modern ion analyzers is especially easy. After calibrating the sensor with standard solutions, the instrument can automatically calculate the ion concentration of the sample, display the results, print them and send them to a computer.

Incremental methods

Whereas in direct potentiometry the ISE potential is measured only once, incremental methods are based on repeated measurements, and the ion concentration is determined from the differences of these measured potentials. Incremental methods comprise addition and subtraction procedures. They are subdivided into single and multiple incremental methods. For single increment addition methods, a small amount of analyte ion standard solution is added to a large amount of sample solution, or a small amount of sample solution is added to a large amount of analyte ion standard solution.
Multiple incremental methods refer in practice to multiple standard

Incremental methods

- Standard addition (single or multiple)
- Standard subtraction
- Sample addition
- Sample subtraction

additions, i.e. the addition of standard solution is repeated several times, typically 3 to 4 times.

Subtraction is based on precipitation or complexation (masking) of the analyte ion requiring additional reagents to be used. Subtraction methods are less frequently applied.

The increment size is selected to achieve an electrode potential change of approximately:
- 30 mV for monovalent ions, e.g. K^+, Na^+, F^-
- 10 mV for bivalent ions, e.g. Ca^{2+}, Cu^{2+}, S^{2-}

The result sample concentration is calculated taking into account the initial volume of sample or standard solution, the added volume of standard or sample and its concentration, and the slope of the ISE, which is obtained from a calibration curve. The slope is factored out if more than one increment is made.

Modern ion meters and titrators provide built-in functions to perform incremental methods and an automatic result evaluation. The pre-programmed methods are ready for instant use, but can also be modified according to the actual need. Therefore, users easily follow the respective instructions and do not need to care about the calculation formula.

METTLER TOLEDO offers several instruments suitable for ion concentration measurements.

Single standard addition

The addition of the standard solution causes the analyte ion concentration in the sample to increase.

Available	Sample solution; defined volume of 50 to 100 mL
Added	A defined volume of 0.5 to 10 mL of the analyte ion standard solution The concentration of the standard must be 10 to 100 times higher than the expected sample ion concentration
Measured	Electrode potential before and after the addition

Single sample addition

The addition of the sample solution causes the analyte ion concentration to increase in the standard of low concentration.

Available	Analyte ion standard solution; defined volume of 50 to 100 mL The concentration of the standard must be 1/100 to 1/10 of the expected sample ion concentration
Added	A defined volume of 0.5 to 10 mL of sample solution
Measured	Electrode potential before and after the addition

Double or multiple standard addition

Several additions of the standard solution increase the analyte ion concentration in the sample stepwise.

Available	Sample solution; defined volume of 50 to 100 mL
Added	A defined volume of 0.5 to 1 mL of the analyte ion standard solution The concentration of the standard must be 10 to 100 times higher than the expected sample ion concentration Two or several (typically 3 to 4) additions of the same amount
Measured	Electrode potential at the beginning and after each addition

Standard subtraction

The addition of the standard solution causes part of the analyte ions in the sample solution to be precipitated or complexed. Thus, the analyte ion concentration in the sample solution decreases.

Available	Sample solution; defined volume of 50 to 100 mL
Added	A defined volume of 0.5 to 10 mL of a standard solution that complexes or precipitates the analyte ion The standard concentration must be 10 to 100 times higher than the sample The amount of standard solution added must be such that the measurement ion is not completely precipitated or complexed (to remain measurable)
Measured	Electrode potential before and after the addition

Sample subtraction

The sample is added to an ion X standard solution. The analyte ion complexes or precipitates the ion X. As a consequence, the ion X concentration in the standard solution decreases. The ISE is selective for the ion X but not for the analyte ion.

Available	Ion X standard solution; defined volume of 50 to 100 mL The ion X concentration of the standard should be 1/100 to 1/10 of the expected sample analyte ion concentration
Added	A defined volume of 0.5 to 10 mL sample solution The amount of sample added must be such that the measurement ion is not completely complexed or precipitated
Measured	Electrode potential of ion X before and after the addition

Titration methods

Modern automatic titrators are also well-suited to perform incremental ISE methods. In addition to ion meters, autotitrators offer the option to execute the increments precisely and automatically with the titrator's burette. Hence, all steps of an incremental method can be automated including the result calculations. Automation reduces manual operation errors considerably and can increase efficiency.

1.9 Advantages of the measurement procedures

A brief comparison of the two measurement techniques shows advantages and limitations. Evaluation of the most suitable procedure depends on the application, the required result quality, the available analysis time, and the analysis equipment.

	Advantages	**Limitations**
Direct measurements	• Simple measurement • Basic ion meter is sufficient • Fast (1 measurement only) • Can be easily automated	• Needs calibration curve • Need for ISA solutions to compensate for ionic strength variation • Matrix effects • Sample and standard should have same temperature
Incremental methods	• No calibration required (in case of multiple additions) • Reduced or no matrix effects • Reliable and correct measurement down to the limit of detection • ISA solutions may be omitted or reduced • No influence of temperature differences • Efficient automation possible with modern titrators	• Exact sample volume has to be used • Precise increment dosing required • Approximate concentration must be known to estimate increment size and concentration • Needs more time (two or more measurements)

Table 1.5: Comparison of measurement procedures.

1.10 Low-level measurement techniques

Low level techniques are used for samples with a low ion concentration, typically less than 1 mg/L or 10^{-5} mol/L. At such low concentrations, any interfering and disturbing influence on the ISE measurement has to be carefully avoided.

Furthermore, low level techniques can be applied to some ISEs only. Refer to the ISE operating instructions to check the feasibility, the recommended low-level setup and measurement hints.

As a summary, accurate low-level results require the following conditions to be met:

- The ISE is calibrated with at least three calibration standards that bracket the expected sample concentration.
- Appropriate ISA solution is used for standards and samples.
- Longer measurement time is needed, because the electrode response time is slower.
- All standards and samples are stirred at a uniform rate. (Applies for all ISE measurements in general.)
- Plastic labware has to be used for all low-level potassium measurements.

2. What is Typically Measured

Ion-selective electrodes are being used in a wide range of applications. Measurement purposes include research projects, education tasks, production monitoring and quality control. Sources almost from "A to Z" are the samples' origins.

2.1 Typical applications in selected industrial segments

Agriculture	Nitrate, potassium, calcium and chlorides in soils and plant materials; nitrate in fertilizers
Biomedical and clinical labs	Calcium, potassium and chloride in serum, blood and other body fluids; fluoride in skeletal and dental structures
Beverages	Sodium and chloride in fruit juices and beer; potassium in fruit juices; fluoride in soft drinks, tea, beer, etc.
Chemistry	ISEs for incoming material inspection, quality control and effluent's monitoring
Detergents	Calcium and barium to study the effects of detergents
Education	Undergraduate analytical chemistry training; experiments on activity coefficient, solubility, equilibrium, etc.
Electroplating	Fluoride and chloride in edging baths; copper, zinc, etc.
Environment	Pollution monitoring of fluoride, cyanide, chloride and sulfide
Explosives	Fluoride, chloride and nitrate in explosives and their combustion products
Food	Nitrate in meat and meat preservatives; sodium and chloride in meat, fish, dairy products, etc.; calcium in milk and dairy products; nitrate in vegetables
Mining	Urinary fluoride monitoring of aluminum production workers
Paper and pulp	Sulfide and chloride in pulping liquors, recovery cycles and effluents
Pharma	Fluoride concentration in samples from research and quality control; application of other ISEs
Power generation	Chloride, sodium and calcium in effluents; fluoride in nuclear fuel reprocessing
Water	Potassium, sodium, calcium, chloride in drinking water, brewing water, etc.; nitrate in waste water and effluents

Table 2.1: ISE applications in industrial segments.

2.2 Selected application examples

The following table summarizes the measurable ions, which ion-selective electrodes to use, sample examples, the proposed method type and some sample preparation hints.

Analyte ion	ISE	Sample	Method	Sample preparation hints
Aluminum	Fluoride	Metals, alloys, solutions	T	Dissolve in HCl, adjust to pH 4
Ammonium	Ammonium	Biological materials	D, A	Extract or macerate
		Beer	A	
		Water (natural, waste, boiler feed, fish tanks, etc.)	A	
Bromide	Bromide	Soils, plant material	D	Extract with 2M $NaNO_3$
		Wine	A	Add H_3PO_4 and KNO_3 buffer solution
Calcium	Calcium	Milk	A	Dissolve in 0.1M $NaNO_3$
		Soil	D	Extract with sodium acetate solution pH 8.2, filter, measure in filtrate
		Sugar solutions	D, A	Make up standards in sucrose solution
		Water	D	
	Cupric	Milk, dairy products	T	Add ammonia solution. Digest dairy samples first in HCl.
Chloride	Chloride	Biological fluids, sweat	D, T	
		Food	D	Solids: extract with H_2O or disperse sample in hot HNO_3
		Lubrication oils	D	Extract with H_2O
		Pharmaceuticals	D, T	
		Soil	D, T	Leach sample with H_2O
		Water, sea water	D	Sea water: calibrate ISE in artificial sea water
Cupric	Cupric	Plating solution	T	Titrate with 0.1 M EDTA
		Water, waste water	D	
Explanations		Method	D A T	Direct measurement Addition (incremental) methods Titration

Analyte ion	ISE	Sample	Method	Sample preparation hints
Cyanide	Cyanide	Biological samples	D	
		Pharmaceuticals	D	Measure at pH 11
		Water (drinking water, industrial water, waste water)	D	Sulfides interfere with the measurement
Fluoride	Fluoride	Air, gases	D	Collect fluoride on filter paper, extract with H_2O, add TISAB
		Biological samples (plants, soils, etc.)	A	Extract or digest sample
		Body fluids (saliva, urine, serum)	D	Add TISAB
		Electroplating baths	A	Add TISAB
		Milk	D	Add TISAB
		Teeth, dental plaque	D	Dissolve/suspend in $HClO_4$, add sodium citrate buffer
		Toothpaste	D	Add TISAB
		Water (drinking water, natural water, waste water)	D	Add TISAB
		Wine	A	Add TISAB
Iodide	Iodide	Biological samples	D	Extract sample
		Food	D	Extract sample
		Pharmaceuticals	D	
		Water	D	
Lead	Lead	Water, waste water	D	Add methanol-formaldehyde solution
Magnesium	Cadmium	Water	T	Titrate with EDTA, add Cd-EDTA as an indicator
Nitrate	Nitrate	Baby food	D	Extract with H_2O
		Fertilizer	D	Extract with diluted H_2SO_4
		Food, meat	D	Cut or grind sample, extract with H_2O
		Soil	D	Extract
		Water (drinking water, natural water, waste water, sea water)	D	
Explanations		Method	D A T	Direct measurement Addition (incremental) methods Titration

Analyte ion	**ISE**	**Sample**	**Method**	**Sample preparation hints**
Potassium	Potassium	Body fluids (saliva, serum, urine)	A	
		Fertilizer	A, D	Extract with acetate buffer solution
		Food (fruit juice, milk, vegetable juice)	D	
		Wine	D	
Silver	Silver	Plating bath (cyanide)	A	Dilute sample
		Low level silver solutions	D	
Sodium	Sodium	Biological material, plants	D	Extract sample
		Drugs	D, A	
		Food (milk, fruit juice, beef broth, tea/infusion)	D	
		Serum	D	
		Water (drinking water, boiler water, sea water)	D	Sea water: calibrate ISE in artificial sea water
		Wine	D	
Sulfate	Cupric	Ethanol (fuel blending agent)	T	Add diluted $HClO_4$ solution
Sulfide	Silver	Cigarette smoke	D	Scrub smoke with solution of 0.2M ascorbic acid and 2M NaOH
		Soils	D	
		Water	D	Add sulfide anti-oxidant buffer (SAOB)
		Wood chips	D	Extract with SAOB
Zinc	Cupric	Electroplating baths	T	Complexometric titration with EDTA
Explanations		Method	D A T	Direct measurement Addition (incremental) methods Titration

Table 2.2: Application examples of ISEs.

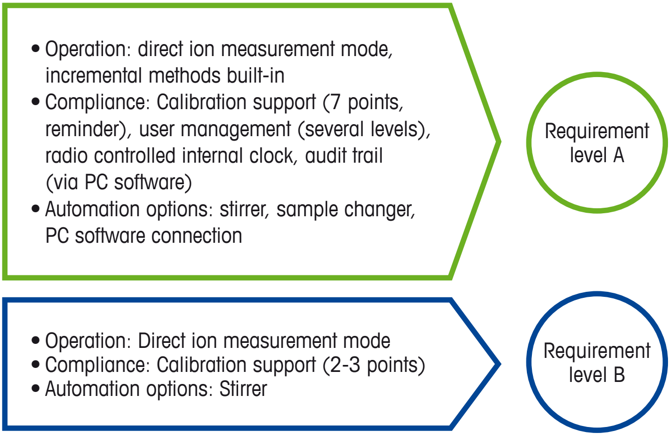
3. The Meter-Sensor-Solution System

Reliable and fast ion concentration determinations depend on an appropriate measuring system. Five steps guide you to the right system for your applications.

3.1 Select the ion meter

Users of ion meters have different needs and requirements to cover. Hence, manufacturers offer several meters to match them. Rather simple meters provide few functionalities for basic applications. High performance meters come with a higher number of functionalities, including incremental procedures, built-in methods with automatic result calculations, compliance support and automation. Depending on the needs, the customer has to choose the appropriate meter requirement level.

Typical requirements **Requirement level**



- Operation: direct ion measurement mode, incremental methods built-in
- Compliance: Calibration support (7 points, reminder), user management (several levels), radio controlled internal clock, audit trail (via PC software)
- Automation options: stirrer, sample changer, PC software connection

Requirement level A

- Operation: Direct ion measurement mode
- Compliance: Calibration support (2-3 points)
- Automation options: Stirrer

Requirement level B

Figure 3.1: Typical requirements and respective levels.

Another criterion is the place of use: A benchtop meter is used in the laboratory. For field use, a portable meter is recommended.

3.2 Choose the sensor

Depending on the analyte ion, the respective ion-selective electrode is chosen. However, when ISEs are applied to titration for indication purposes, ionic species other than the selected ion can be analyzed. See ISE application overview in chapter 2.2.

For many ions, combined and half-cell ISEs are available. It is up to the user to select the most advantageous electrode(s) for the required application.

Combined ion-selective electrodes	Half-cell ion-selective electrodes plus reference
• Easy to operate • Easy to maintain • 1 sensor only, 1 cable only • Suitable for small sample volumes	• Reference electrode selectable to match sample matrix • Reference electrode independent of ISE life time • Same reference electrode for all ISEs

Table 3.1: Some characteristics of ion-selective electrodes.

3.3 Choose the solutions

Ionic strength adjustment (ISA) solutions

It is important for ion analysis with ISEs to use ISA solutions. ISA solutions, total ionic strength adjustment buffers (TISAB) and other reagents keep the ionic strength of different samples and of the standards relatively constant. They also contribute to diminish interferences and other matrix effects (chapter 1.7).

Depending on the ion to be measured, the respective ISA solution is chosen. ISA solutions are added in the same proportion to sample and standards. See the ISE operating instructions for the selection of the ISA solutions.

In most cases, the addition of a few milliliters ISA solution is sufficient to adjust the ionic strength of samples and standards. The composition of ISA solutions varies considerably depending on the ISE in use. For more details refer to the ISE operating instructions or the corresponding literature.

Example 1: for the calcium determination, it is sufficient to adjust the ionic strength only, e.g. by the addition of potassium chloride. Hence, the calcium ISA contains one component only.

Example 2: TISAB II or TISAB III solutions, which are used for fluoride measurements, adjust the ionic strength, the pH value and complex interfering ions. Therefore, sodium and chloride ions, pH buffering compounds such as citrates or acetates, and complexing agents make up the TISAB solutions.

Reference electrolytes

Use the correct electrolyte according to the operating instructions. The reference electrolyte has to be refilled periodically. The minimum filling level has to be higher than the sample level.

Calibration standard solutions

For ISE measurements, use at least two calibration standards that encompass the expected sample concentrations.
The accuracy of the calibration results of ISEs depends on the precision of the standard solutions. Hence, it is recommended to use either ready-to-use standard solutions or to prepare the required concentrations with a serial dilution. See chapter 4.2.

Figure 3.2: Selection of solutions for ISEs.

ISE standard solutions, ISA solutions and electrolytes are available from METTLER TOLEDO.
▶ **www.mt.com/BuffersAndMore**

3.4 Helpful accessories

Accessories such as stirrer, sample changer, temperature probe, printer, and data transfer options complete the system. They contribute to safe and fast workflows by supporting users through the entire measurement procedure.

Accessory	Benefits
Stirrer	Automated stirring, uniform and constant stirring speed for all samples and standards
Sample changer	Automated ISE measurement, less operator working time involved
Printer	Results documented on paper
Data transfer option	Automatic data transfer, automatic data storage, connection to laboratory management system, enhanced compliance support

Table 3.2: Accessories and their benefits.

Figure 3.3: A compact printer connected to a typical multi-parameter ion meter.

3.5 Installation, calibration and maintenance

By having the equipment professionally installed by factory-trained service technicians, users are assured that the system is up and running perfectly from the start. METTLER TOLEDO offers several levels of installation packages, which are suitable for different industries and applications.

Once the system is in use, periodic preventive maintenance is recommended to ensure continuously accurate and reliable operations. Combined with regular instrument calibration, safe results can be ensured and costs of down-time avoided.

METTLER TOLEDO helps customers to understand the risks involved in ion measurement and recommends ways to prevent those risks becoming problems, with the Good Electrochemistry Practice™ (GEP) program.

▶ **www.mt.com/GEP**

Figure 3.4: Regular instrument calibration ensures reliable measurement results.

4. Good ISE Practice

This chapter presents some hints and recommendations for the daily use of ISEs. They are based on generally accepted handling and operational rules and support you in reaching a good practice level.

4.1 Sample preparation for ISE measurement

ISE measurements are carried out in liquid samples. Hence, solid samples need to be dissolved. The analyte ion can often be extracted. Samples may also need dilution to reach the linear range of the ISE. Use deionized water for dissolution and extraction.
Finally, add the ISA solutions to samples and calibration standards.

4.2 ISE preparatory steps

Prior to its use, an ion-selective electrode needs conditioning.Soaking it for 10–15 minutes in a 1 mg/L or 10^{-4} mol/L standard solution is a general procedure. After dry storage, carry out soaking for several hours, typically overnight. Then, prior to the measurements keep ISE for 15 minutes in deionized water. For more details, please refer to the operating instruction of the ISE.
Fill the reference electrode with electrolyte according to the operating instructions.

- The filling level must be higher than the sample level.
- The electrolyte filling hole must be open during measurements.

For calibration, METTLER TOLEDO offers a range of ready to use standard solutions. If you need different standards, serial dilution is the best method for their preparation. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on.

Serial dilution example

To prepare a 100 mg/L standard: Pipette 10 mL of the 1000 mg/L standard into a 100 mL volumetric flask. Fill up to the mark with deionized water and mix well.

To prepare a 10 mg/L standard: Pipette 10 mL of the 100 mg/L standard into a 100 mL volumetric flask. Fill up to the mark with deionized water and mix well.

4.3 Measurement and calibration – stirring and rinsing

Take a defined volume of samples and standards. Add the appropriate amount of ISA solution to all of them. Stir samples and calibration standards at a uniform rate. Apply gentle stirring to ensure good mixing. A strong vortex should be avoided, as it will aspirate air bubbles.

Immerse the ISE properly, at least 1 cm. Make sure that the reference junction is completely immersed.

Always rinse the electrode with deionized water between measurements to prevent sample carryover. Shake the electrode gently to remove the rinsing water. Dab dry with low lint tissue. Do not wipe or rub the electrode sensing element.

Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. Recalibrate the electrode, when the following deviation occurs:

- Solid state membrane ISE: the value has changed by more than 2%.
- Polymer membrane ISE: the value has changed by more than 4%.

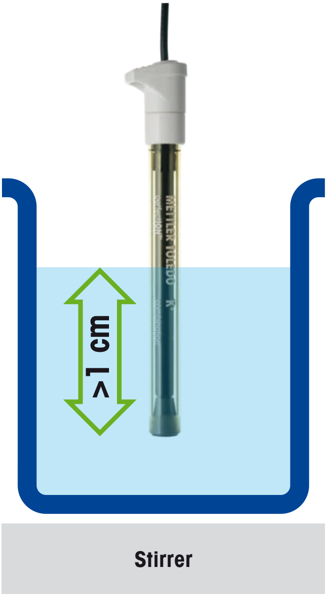


Figure 4.1: ISE position in sample.

4.4 Easy system check

The easy system check verifies the proper performance of the ion-selective measuring system when work is taken up. When carried out during measurement series, the check confirms on-going correct performance of the meter and the ISE.

1. Prepare the following solutions: 50 mL of 10^{-3} mol/L and 50 mL of 10^{-1} mol/L ion standard solution, both with corresponding ISA solution added. It is also possible to use a 10 and a 1000 ppm standard instead.
2. Read the mV value of the 10^{-3} mol/L or 10 ppm ion standard solution.
3. Then, after rinsing, read the mV value of the 10^{-1} mol/L or 1000 ppm ion standard solution.
4. Compare the mV reading with the data on the ISE manufacturer data sheet. The mV readings should not differ by more than 30 mV.
5. Calculate the mV difference between the two standard solutions. For monovalent ions, expect a difference of 120 ± 30 mV. For bivalent ions expect a difference of 60 ± 15 mV.

The system has passed the check, if absolute values and the difference match the expectations.
If the system has failed, follow the troubleshooting procedures. Hints for troubleshooting are explained in chapter 5 of this guide.

4.5 Maintenance and handling of ISEs

The different membranes of ISE require different handling and operation. In all cases, the handling of the sensing membranes has to be careful to prevent any mechanical damage or chemical deterioration. Do not touch polymer membranes. Set a low stirring speed to avoid jumping magnetic stirrer bars.

Membrane type	**Measures after each sample**	**Performance restoring measures**
Solid state	• Rinse with deionized water, and if not sufficient, rinse with ethanol to remove deposits • Dab dry with low lint tissue	• Keep membrane surface smooth and shiny • Only if there are marks: Gently polish surface with fine emery paper
Glass	• Rinse with deionized water, and if not sufficient, rinse with ethanol to remove deposits • Dab dry with low lint tissue • Keep glass membrane hydrated / do not store dry	• Renew membrane surface with reactivation solution
Polymer	• Rinse with deionized water • If deionized water is not sufficient to clean, rinse briefly with 1:1 solution of ethanol and water. Rinse with deionized water immediately afterwards • Do not immerse ISE in organic solvents	• Replace membrane if broken

Table 4.1: Maintenance measures for ISEs.

4.6 Storage of ISEs

Guided by practical reasons and ISE shelf life considerations, the following storage conditions are recommended. Refer to the respective ISE operating instructions for more details.

Storage period	Storage measures
Short period storage	Store wet • Keep the electrode in 10^{-2} mol/L or 100 mg/L standard solution • Do not add ISA solution
Storage longer than one week	Store dry • Drain the electrode and flush the reference chamber with deionized water • Protect the membrane from physical damage, e.g. put the detachable sensing module in its vial ISEs with glass membrane: store wet only

Table 4.2: General storage conditions.

Reference electrodes: store the reference electrode without the bridging electrolyte.

5. Troubleshooting

When problems occur, follow a systematic procedure to locate the sources of error. Thoroughly check the four components of the measuring system one by one. Refer to the manufacturer's data.

System check

The easy system check as explained in chapter 4.4 is the initial step to identify the problem and restore the original level of performance. See also chapter 4.5 for ISE maintenance.

Hints for troubleshooting

The following table contains hints to solve frequently encountered problems. The hints are grouped according to the source of the problem.

Meter	• Defective instrument: Check the meter performance. See the meter or titrator user guide. Is the meter properly connected and grounded? Apply shorting clip. If this does not set the potential to 0 mV, call service. • Static electricity present: Wipe plastic parts on the meter or titrator with a detergent solution.
Electrode	• Electrode not properly connected to meter: Unplug and reconnect the electrode to the meter. Clean connector and meter socket. Replace cable if needed. • No reference filling solution added: Fill the electrode up with filling solution. Refer to the ISE instructions. • Incorrect reference filling solution used: Refer to the ISE instructions to verify that the correct electrolyte was used. • Electrode is dry or dirty or reference junction is clogged: Refer to the maintenance section of the ISE instructions for electrode cleaning and flushing advice. Unblock reference junction. • Air bubble on sensing module: Remove air bubble by re-immersing the electrode in solution.

Application	• Standards are contaminated or prepared incorrectly: Prepare fresh standards. Use valid reagents. • ISA not used or incorrect or expired ISA used: ISA must be added to all standards and samples in the same ratio. See chapter 3.3. Refer to the ISE instructions. Check expiry date. • Ion concentration and/or pH value out of range: Adjust sample. Adjust pH. • Interferences present: Avoid or remove interfering substances. Add ISA. • Samples and standards at different temperatures: Allow solutions to reach the same temperature. • Temperature increases during measurement: Avoid heat transfer from the magnetic stir plate. Place a piece of insulating material (e.g. Styrofoam or cardboard) between plate and sample beaker. • Temperature exceeds the admitted temperature range of the ISE: Refer to the ISE instructions. Cool accordingly.
Technique	• Review operating procedures: Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode. • Review calibration procedure: If working with low-level samples, apply a low-level calibration procedure. • Review method: Replace a direct measurement method with a standard addition method.

Table 5.1: Hints for troubleshooting.

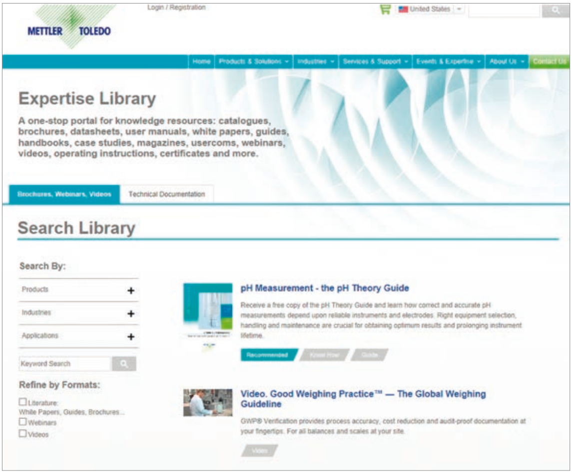
6. For More Information

A variety of documents are listed below for further reading and reference regarding ion selective electrodes, ion and pH meters, as well as related analysis techniques.

Expertise Library

METTLER TOLEDO's library is a one-stop portal to access knowledge resources such as guides, application brochures, literature, webinars, products information and more.

▶ **www.mt.com/Library**



Expertise Library

A one-stop portal for knowledge resources: catalogues, brochures, datasheets, user manuals, white papers, guides, handbooks, case studies, magazines, usercoms, webinars, videos, operating instructions, certificates and more.

Search Library

pH Measurement - the pH Theory Guide

Receive a free copy of the pH Theory Guide and learn how correct and accurate pH measurements depend upon reliable instruments and electrodes. Right equipment selection, handling and maintenance are crucial for obtaining optimum results and prolonging instrument lifetime.

Video. Good Weighing Practice™ — The Global Weighing Guideline

GWP® Verification provides process accuracy, cost reduction and audit-proof documentation at your fingertips. For all balances and scales at your site.

Webinars

METTLER TOLEDO provides web-based seminars (webinars) on different topics. You can participate in on-demand webinars at a convenient time and place for you. The following webinars for pH are available free of charge:

- How to calibrate pH
- Temperature effects in pH measurements
- pH measurement errors

▶ **www.mt.com/webinars**

Guidebooks of METTLER TOLEDO perfectION™ ISEs
Comprehensive guidebooks for perfectION combined ISEs are available in English and many other languages.
Calcium, chloride, copper, cyatnide, fluoride, iodide, lead, nitrate, potassium and silver/sulfide.
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perfectION™ Guidebook
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Combination Fluoride Electrode
Successful Ion Measurement
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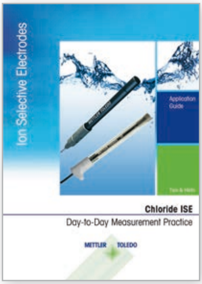
Day-to-day measurements brochures
The brochures Day-to-Day Measurement Practice are available in English for the following ISEs: barium, calcium, chloride, fluoride, nitrate and potassium.
Go to
▶ **www.mt.com/Library**


Ion Selective Electrodes
Application Guide
Tips & Hints
Chloride ISE
Day-to-Day Measurement Practice
METTLER TOLEDO

Related Guides
All you need to know. Elaborate contents about pH or conductivity provide applications overview, tips and tricks on proper measurement, sensor handling and maintenance as well as an introduction to the theory.

A guide to pH measurement	51300047
A guide to conductivity measurement	30099121

Good Electrochemistry Practice™
Know the Risks of Your pH Measurement

Measuring pH in the laboratory is a common analysis, but so many things can go wrong. The same goes for conductivity, ion concentration, dissolved oxygen and redox. Good Electrochemistry Practice™ is about guiding you through the whole product lifecycle, detecting possible risks and finding the right tools to address these issues and ascertain good results.

- Preservation of the accuracy and precision of results
- Compliance with regulations
- Minimization of risks
- Increased productivity and reduced costs
- Protection of investment

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For more information

Mettler-Toledo GmbH, Analytical
Heuwinkelstrasse 3
8606 Nänikon, Switzerland
Tel. +41 44 944 47 47

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