WHITE PAPER

# Overcoming difficulties in ion measurement: Tips for standard addition and direct measurement

The amount of ions belonging to different elements in a sample tells a certain story. In foods and beverages, specific limits for different ions are set to safeguard health and ensure a minimal nutrient content. In soil and environmental water sources, increased levels of certain heavy metal ions can suggest a pollution event has occurred. In the ultrapure water used in many manufacturing processes, the presence of any ions above a threshold indicates either the source water is unfit for use, or that the filter system requires maintenance.

Ion measurement can be conducted in several different ways, e.g., ion chromatography (IC), inductively coupled plasma optical emission spectrometry (ICP-OES), or atom absorption spectroscopy (AAS). Each of these are well-established, widely used methods in analytical laboratories. However, the initial costs are relatively high. In contrast, ion measurement by the use of an ion-selective electrode (ISE) is a promising alternative to these costly techniques. This White Paper explains the challenges which may be encountered when applying standard addition or direct measurement, and how to overcome them in order for analysts to gain more confidence with this type of analysis.

## INTRODUCTION

In 1889, Walther Nernst developed the «**Nernst equation**» which made the evolution of pH measurement by potentiometric sensors a possibility. For nearly 70 years, pH determination was the only analysis where this equation was of importance. At the beginning of the 1960's it was observed that cuts of lanthanum fluoride crystals showed excellent selectivity towards fluoride ions [1–2]. Thus, the first ion-selective electrode next to the pH electrode was built. Since then, ion-selective electrodes were gradually developed by discovering new crystal, glass, gas permeable membrane, and polymer materials. Some of these different ISEs are mentioned in **Table 1**.

Table 1. Overview of assorted ion-selective electrodes and their capabilities [3].

| Membrane Material | Ions |
|---|---|
| Crystal | $Ag^+$, $Cu^{2+}$, $Pb^{2+}$, $Br^-$, $Cl^-$, $CN^-$, $F^-$, $I^-$, $S^{2-}$ |
| Polymer | $Ca^{2+}$, $K^+$, $Na^+$, Surfactants, $NO_3^-$ |
| Glass | $Na^+$, $H^+$ |
| Gas permeable membrane | $NH_4^+$ |

Performing measurements with ion-selective electrodes might be challenging at times, but when certain important points are considered, analysis of the specific ion of interest can be achieved easily. In the following few sections, general tips for potentiometric ion measurement are given, as well specific ones for standard addition and direct measurement.

## GENERAL HINTS

Ion measurement is very easy to perform. To ensure both long-term user satisfaction and the accuracy of the analysis, the manufacturer's instructions must be followed. The following points give an overview of some common questions and problems.

### – MEASURING RANGE OF ELECTRODE

Each type of electrode type has its own specific measuring range, which usually encompasses a linear range of about six decades of mol/L. The linear range in **Figure 1** is drawn for the case c where no interferences are present. In this region, the signal is proportional to the concentration and follows the Nernst equation. In the high and low level concentration regions the curve flattens and the potential difference becomes smaller, which is visualized in **Figure 1** for case c. Interfering ions reduce the linear range and cause therefore a decrease of the measuring range.

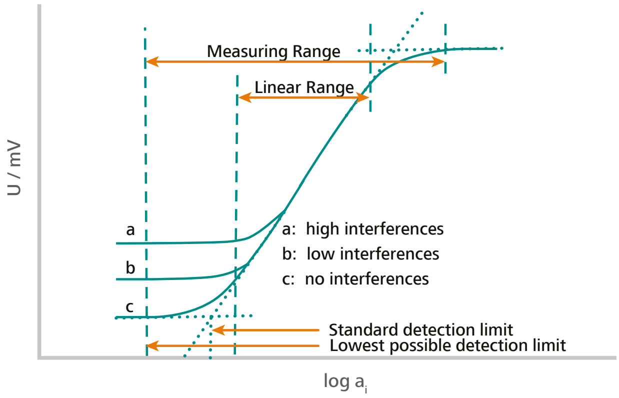

Figure 1. This illustration explains how the measuring range and the linear range are defined. The **measuring range** is defined from the two points located in the high and low concentration range where no potential change is observed anymore. This means either the concentration is too low, or the sensor is saturated. The **linear range** is defined as the range where the signal evolves linearly with the activity (concentration) of the ion according to Nernst.

Therefore, it is recommended to measure in the linear region to obtain precise and reproducible results. However, an ion concentration measurement in the non-linear (flattened) region by direct measurement is also possible if the sensor is calibrated in this narrow range. Electrodes normally have a measuring range between $10^{-6}$ to 1 mol/L. Depending on the type of ion-selective electrode used, the measuring range might extend up to 8 mol/L and down to $10^{-8}$ mol/L. Before selecting ion measurement as the method of choice, the analyst must be certain that the electrode is able to measure in the concentration range of the sample.

## INTERFERING IONS

The pH electrode was the first ion-selective electrode built. This electrode exhibits an excellent linear range of 14 decades, and is selective for $H^+$. In contrast, most other ion-selective electrodes are not that selective for the measuring ion.

There are two different types of interfering ions: reversible and irreversible. Irreversible interfering ions bind to the membrane material and react with it, or they form complexes and precipitate with the measuring ion so that it is unavailable for further analysis. If the irreversible interfering ion is reactive towards the membrane, its presence should be avoided as otherwise the ISE will be destroyed. Reversible interfering ions exhibit cross-sensitivities due to both similar size and electronic properties as the measuring ion. These can bind to the membrane material as well, and contribute to the signal, giving erroneous results.

As cross-sensitivities are common in ion measurement, the Nernst equation was expanded to the so-called **Nikolsky equation**:

$$U = U_0 \pm \frac{2.303 \times R \times T}{n \times F} \times \log(a_i + \sum k_{ij} \times a_j^{nm})$$

$U$: measured potential between ISE and reference electrode in mV
$U_0$: measured potential between ISE and reference electrode at c(ion) = 1 mol/L in mV
$R$: universal gas constant ($R = 8.314$ J/(mol·K))
$T$: temperature in Kelvin
$F$: Faraday constant (96485 C/mol)
$n$: electrical charge of the ion
$a_i$: activity of the ion to be measured
$k_{ij}$: selectivity constant (ion to be measured / interfering ion)
$a_j$: activity of interfering ion
$m$: electronical charge of the interfering ion

At present, this equation is implemented in most ion meters for direct measurement.

## CONDITIONING OF THE ELECTRODE

Ion-selective electrodes are normally delivered dry, independent of the membrane material used. To activate the measuring membrane, it is necessary to condition the electrode first. Conditioning ensures that the equilibrium of the measuring ion in the membrane is maintained and therefore an accurate measurement is possible. It is proposed to use an ion standard solution with a concentration of c(ion) = 0.01 mol/L as the conditioning solution.

Since reliable ion measurements require a stable equilibrium of the measuring ion in the membrane, the ISE should also be conditioned in between measurements. In this case, the conditioning solution depends on the concentration of the measuring ion within the sample. Further information regarding the correct conditioning solution can be found in the manufacturer documentation for specific ion-selective electrodes or applications.

## TOTAL IONIC STRENGTH ADJUSTMENT

The total ionic strength adjustment is needed because the ion measurement depends not on the concentration of the measuring ion in solution, but on the activity thereof. This parameter varies with the concentration of ions present in the solution, and also with the pH which influences the dissociation of specific molecules. Therefore, as a bare minimum, it is necessary to maintain a constant ionic background which can be achieved by the addition of ionic strength adjuster (ISA).

Depending on the measured ion, a fixed pH value is necessary as well. In that case a total ionic strength adjustment buffer (TISAB) is used. ISA and TISAB solutions normally contain a relatively high concentration of salt which does not interfere with the measurement. Recommendations for specific ISA and TISAB solutions can be found online or in the manual provided for the ion-selective electrode.

Table 2. Examples of ISA/TISAB solutions for different ionic measurements and information regarding where to find the analysis procedure.

| Ion to be measured | ISA/TISAB for 100 mL solution | Further information about procedure |
|---|---|---|
| Fluoride ($F^-$) | 0.45 g CDTA (Komplexon IV) suspended in deionized water and dissolved with c(NaOH) = 10 mol/L<br>5.84 g NaCl<br>5.75 mL glacial acetic acid | **Metrohm Application Bulletin 082** |
| Potassium ($K^+$) | 0.584–5.844 g NaCl depending on $K^+$ concentration (c(NaCl) = 0.1–1 mol/L) | **Metrohm Application Bulletin 134** |
| Sodium ($Na^+$) (Glass membrane) | 12.11 g Tris(hydroxymethyl)aminoethane (c(Tris(hydroxymethyl)aminoethane) = 1 mol/L)<br>or<br>7.50 mL Triethanolamine | **Metrohm Application Bulletin 083** |
| Sodium ($Na^+$) (Polymer membrane) | 14.70 g $CaCl_2 \cdot 2\,H_2O$ | **Metrohm Application Bulletin 083** |
| Ammonium ($NH_4^+$) | 40 g NaOH (c(NaOH) = 10 mol/L) | **Metrohm Application Bulletin 133** |

## – CLEANING OF THE ELECTRODE

After each measurement, the electrode is cleaned thoroughly with deionized water. Organic solvents should not be used for cleaning, as they may reduce the lifetime for ion-selective electrodes with crystal membranes and destroy ion-selective electrodes with polymer membranes.

When measuring in very low concentration samples, allow the electrode to stand for 10 minutes in deionized water or ISA / TISAB prior to beginning the next measurement. Otherwise, the ions bound to the electrode membrane material from the previous measurement might diffuse out and thus falsify the signal and the obtained result of subsequent samples. The deionized water should be exchanged before each measurement, as diffusion might lead to an enhancement in concentration of the measured ion and therefore contamination of the deionized water.

## – STORAGE OF THE ELECTRODE

The storage requirements of the electrode depends on the time period of storage and the type of the electrode (**Table 3**).

Table 3. Recommendations for the storage of different ISE types.

| Membrane material | Short storage period | Long storage period |
|---|---|---|
| Polymer | Dry | Dry |
| Polymer, combined | In c(ion) = 0.01–0.1 mol/L | Dry, with some residual moisture |
| Crystal | In c(ion) = 0.1 mol/L | Dry, with protective cap |
| Glass | In c(ion) = 0.1 mol/L | In deionized water |

The proper storage instructions are described in the manual included with the ion-selective electrode.

## – ELECTRODE LIFETIME

The lifetime of an ISE depends on the membrane type, sample matrix, and electrode maintenance. Satisfactory electrode maintenance consists of regular cleaning, proper conditioning, and storage as previously outlined in this white paper. Furthermore, it is necessary to exchange the electrolyte of the reference electrode on a regular basis.

As mentioned earlier, the sample matrix can react with the membrane of the ion-selective electrode. The manual of the electrode usually lists which substances should be avoided. For example, organic solvents can destroy the polymer membrane of ISEs, or acetate will interfere the crystal of the lead ISE.

For ion-selective electrodes with a crystal membrane, the membrane can be periodically regenerated by polishing it. The appropriate polishing material and procedure can normally be found in the ISE manual [3]. With good maintenance and without lasting sample matrix influences, these types of electrodes can withstand several years of use in the laboratory.

The lifetime of polymer membrane electrodes is more limited in comparison to those with crystal membranes. Over time, the polymer membrane ages, resulting in a loss of performance. This kind of ISE usually has a «best before» date, during which they deliver their best performance. The electrode should be used until this date, and afterwards Metrohm can ensure such performance for another six months. In general, the mean lifetime for polymer membrane electrodes with normal laboratory use is about half a year.

Be sure to handle the electrode with care and do not touch the membrane with bare fingers as a deposit of fatty film or sweat from the skin can have a negative influence on the performance of the electrode.

## MEASURING MODES

Potentiometric ion measurement can be performed in two different ways: either by standard addition or by direct measurement. Each of these measuring principles has its own advantages and disadvantages, listed in **Table 4** for ease of comparison.

By knowing the properties of your sample and the frequency of your analysis, the right analysis method can be chosen properly.

### – STANDARD ADDITION

For ion measurement by standard addition, the sample is first pipetted into a beaker, then ISA/TISAB is added and afterwards several increments of standard are also added. After each addition, the potential is measured. The ion concentration is then calculated iteratively from the potential difference and volume increment via the method of least squares.

Two types of standard additions are common. Either defined amounts of standard are added to the sample, or the device itself automatically adds the corresponding amount of standard until a previously defined difference in potential is obtained. The second kind of standard addition (defined potential difference) is recommended, as it gives more reliable results.

Table 4. Advantages and disadvantages of standard addition and direct measurement.

| Standard addition | Direct measurement |
|---|---|
| **Advantages** | |
| • Matrix independent<br>• No calibration necessary<br>• Only a single standard is needed<br>• Nearly no user interaction necessary<br>• Electrode is tested with each measurement | • Fast measurement (parameters determined quickly, on average in approximately 60 seconds of measuring time)<br>• Good reproducibility, also at lower concentration ranges |
| **Disadvantages** | |
| • Poor reproducibility in low concentration ranges<br>• Longer determination times (parameters determined within approximately 300 seconds of measuring time) | • A series of standards for calibration must be prepared<br>• Matrix-dependent<br>• Change of electrode properties is only seen during calibration |

Ion measurement by standard addition is chosen as soon as the matrix is unknown and may contain interfering ions that contribute to the measured signal. The total volume of standard added should lie in the region between 10 and 90% of the buret volume, and the number of additions should be at least four (**Figure 2**). Refilling of the buret must be avoided. The added volume should not exceed 25% of the sample volume, as otherwise dilution will falsify the result. Additionally, temperature differences between the standard solution and sample solution should be avoided. The potential difference is also a critical point to consider. It is proposed to add as much standard as required to obtain a voltage difference of at least 12 mV per addition. The calculation of the result is done iteratively by the device itself.

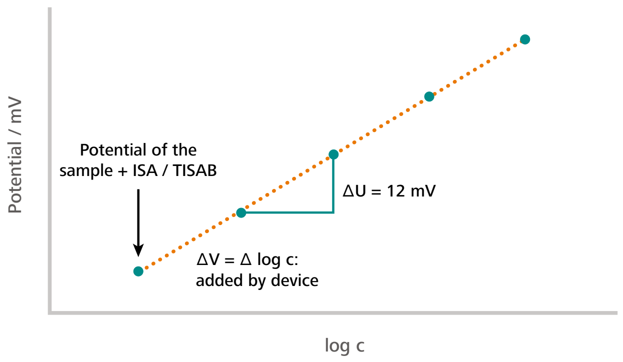

Figure 2. Example of a typical standard addition curve. The first measuring point corresponds to the measured potential of the sample solution (including auxiliary solutions). The subsequent measuring points correspond to the measured potential after each addition of the standard. The initial concentration of the sample is calculated from the measured potential difference in dependence of the added volume increment. The dilution of the sample by auxiliary solutions is considered in the calculations as well.

If the results are not reproducible, the following points have to be checked:

- How much standard is dosed per addition?
- Is the solution stirred while adding standard?
- Is the dosing unit tight?
- Are there air bubbles in the tubing?
- Does the potential measurement between the additions reach a stable potential?
- Is the obtained slope acceptable?

## – DIRECT MEASUREMENT

This type of ion measurement is performed if the sample matrix contains only a few interfering substances and is similar for all samples. Additionally, samples which contain low concentrations of the ion are more suitable for analysis via direct measurement. These samples cause problems with measurement by standard addition: the curve becomes flatter and the evaluation can no longer be done properly (non-linear range).

To determine the concentration of the ion in the sample, a calibration has to be made beforehand. The calibration standard concentrations should be chosen in such a way that they cover the expected concentration of the ion in the sample. The calibration standards consist of a particular concentration of the measuring ion as well as the same proportion of deionized water to ISA/TISAB that is used afterwards in the determination itself. Make sure that the standards are measured from the lowest to the highest concentration to reduce the influence of carry over. The analysis is done by pipetting the standard into a beaker, adding the corresponding amount of ISA/TISAB, and immersing the sensor. The result is then displayed directly in the selected concentration unit. Do not forget to consider the dilution made by adding ISA/TISAB.

Should the results be non-reproducible, the following points can be checked:

- Is the amount of ISA/TISAB the same for all of the standards and for the measuring solution?
- Is the same ratio of ISA/TISAB to sample/standard plus water used for the standard and sample measurements?
- Is the obtained slope of the calibration acceptable?
- Were the standards measured in the correct / defined order?
- Does the calibration range sufficiently cover the sample concentration range?
- Was the electrode properly conditioned between measurements?

## GENERAL POINTS TO CONSIDER FOR ION MEASUREMENT

- Is the standard freshly prepared? Some standards tend to change their concentration with time.
- How old is the electrode? Especially polymer electrodes tend to age quickly. Metrohm proposes a maximum shelf life of 2 years depending on the type of electrode.
- What about the measured value drift? A drift of maximum 1 mV/min should be used.
- Was the sensor properly conditioned? Otherwise the signal and the corresponding results tend to drift.
- The electrode can be checked by immersing the sensor in c(ion) = $1 \cdot 10^{-4}$ mol/L and c(ion) = $1 \cdot 10^{-3}$ mol/L. If the difference in voltage corresponds to at least $47.3/z^*$ mV (at 25 °C) (80% of the Nernst Slope), where $z^*$ is the charge of the ion, then the electrode is ok and can be used.

## SUMMARY

Potentiometric ion measurement by standard addition or by direct measurement is a good alternative to other more costly techniques like AAS, ICP-OES, or IC. The determination is reliable and fast when respecting the conditions of storage, intended use, and measuring range.

# References

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**[2]** Cammann, K. and Galster, H. *Das Arbeiten mit ionenselektiven Elektroden - Eine Einführung für Praktiker*; Springer-Verlag: Berlin, Heidelberg, New York, 1996.

**[3]** Metrohm AG. *Ion-selective electrodes (ISE)*, Metrohm AG: Herisau, Switzerland, 2015. **8.109.8042EN**

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