

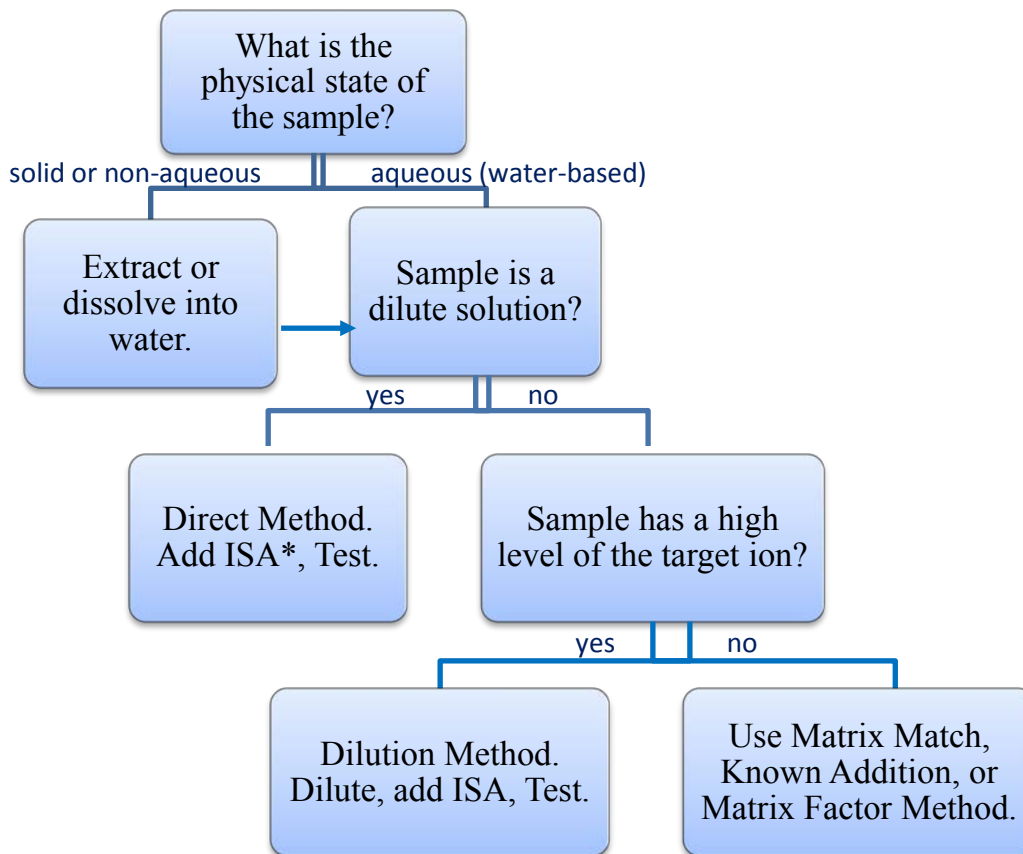


Choosing the Best Method for ISE Measurement of Your Sample: A simple guide for testing ions in various sample types

The Ion Selective Electrode (ISE) is a useful and versatile sensor for testing ions in various types of samples, such as environmental, agricultural, industrial, biotechnical, pharmaceutical, food, wastewater, drinking water, and others. Typical ions of interest include ammonia, fluoride, nitrate, chloride, calcium, sodium, potassium, silver, sulfide, iodide, bromide, lead, cadmium, copper, and others. This Smart Tip will help you decide which measurement technique is best, based on your individual requirements and your application.

How do I choose a suitable ISE method for my sample?

The following flow chart illustrates the general decision making process.



- Ionic Strength Adjustor solution

How does the sample type affect the ISE method that I use for testing?

- **Dilute Aqueous (water) Samples:** Typical dilute aqueous (water) samples can be tested by simple, direct testing. Direct testing is described in the Thermo Scientific Orion ISE User Guide for each ISE, as well as in many regulatory methods that use ISEs. Direct testing involves adding ionic strength adjuster (ISA) solution to standards and samples, calibrating with the standards, and testing the samples.
- **Complex or High Ionic Strength Samples:** Some sample types are not dilute aqueous solutions. Samples that are complex or have a high ionic strength background may require a different approach than the direct test method to obtain the best results. In general, high ionic strength samples are samples of $>0.1\text{M}$ concentration of dissolved ions or samples that may have a conductivity reading of greater than about 10 mS/cm . See below for examples of different sample types.

Examples of Dilute Aqueous Samples

- ultra pure water
- potable water, ground water
- surface (natural) water
- treated wastewater, effluent
- cooling waters, boiler waters
- dilute solutions (e.g., $< 1000\text{ ppm}$)

Examples of Complex or High Ionic Strength Samples

- seawater
- salt solutions, brines (e.g., $>0.5\%$)
- many foods and beverages
- acid bath, alkaline solution (e.g., $>0.3\%$)
- soil extracts ($>0.1\text{M}$ extract solution)
- buffer solutions

To make an accurate measurement using an ISE, a suitable ISE method should be selected according to specific sample conditions.

- For dilute aqueous samples, addition of ISA to both samples and standards normalizes the ion's activity between the samples and the standards to allow for accurate measurements. Therefore, direct testing is a good method choice.
- For complex or high ionic strength samples, addition of ISA may not be sufficient to normalize the ion's activity between the samples and the standards. In that case, choosing an alternate ISE method is recommended for accurate measurements.

What if my sample is a solid or is non-aqueous (not water-based)?

- A solid sample must be prepared, so that the ion of interest is dissolved or extracted into water. For example, a certain type of powder, salt, or tablet sample might be mixed with water to dissolve the ion of interest prior to ISE testing. A soil sample may be dried, crushed, and/or sieved, then extracted into a water or salt solution prior to ISE testing. The extracting solution is chosen to bring the ions of interest into solution, and the extracting solution must not interfere with the ISE test.
- A non-aqueous liquid sample must be prepared so that the ion of interest is extracted into water. For example, an oil sample might be mixed with water or other extracting solution to extract the ion of interest into the water phase. The water phase is then tested. Alternately, the non-aqueous sample might be ashed or subjected to an oxygen combustion bomb preparation (e.g., EPA SW-846 Test Method 5050) to remove the organic matrix. After combustion, the inorganic residue is mixed with water and tested for ions. In some cases, the solid or viscous sample can be added directly to a standard solution and can be tested by analyte addition or subtraction.

ISE Methods Summary: Which method is best for my testing?

Direct Method

- Suitable for dilute, aqueous samples, such as natural waters, potable waters, pure water, dilute solutions, and treated wastewater effluent.
- Follow instructions in the Orion ISE User Guide or your regulatory method.
- Add ISA to samples and standards per ISE User Guide. Calibrate and test.
- Simplest and quickest method.

Dilution Method

- Suitable for high ionic strength samples with high target ion concentration, such as high salt solutions, brine, fluoride in acid bath, calcium in seawater, etc.
- Dilute the sample. Add ISA to diluted samples and to standards per ISE User Guide. Calibrate and test.
- Fairly simple and relatively quick. See Application Note for example.¹

Matrix Match Method

- Suitable for high ionic strength samples of low target ion concentration and well-characterized matrix, such as soil extracts, process or QC samples, seawater, etc.
- Prepare the standards with a composition similar to the samples.
- Add ISA to the samples and the matrix-matched standards per ISE User Guide. Calibrate and test.
- Fairly simple and relatively quick. Good for high volumes of samples. See Application Note for example.²

Known Addition Method

- Suitable for high ionic strength samples of low target ion concentration that do not have an easily matched matrix, such as food, beverage, or waste samples.
- Add known additions of a standard to the sample (or diluted sample). Calibrate and test at same time. Can automate on an Orion meter or use a spreadsheet.
- Once method is established, is fairly simple. Time per test is longer, but no separate calibration curve is needed. See Application Note.³
- Quick for testing frequent, small batches of samples. Don't have to calibrate each time.

Matrix Factor Method

- Suitable for high volumes of samples of high ionic strength, where a matrix factor can be determined, such as QC, production, soil, or seawater samples.
- Test by Direct Method: Add ISA to samples and standards per ISE User Guide. Calibrate and test. Divide results by the matrix factor (MF).
- Once the matrix factor is established, method is simple and quick. To determine the MF, compare ISE results to expected results, spike results, or other method results.

What if a component of my sample is listed as an interference in the ISE User Guide?

For example, if testing for nitrate, the User Guide lists chloride as an interference. According to the Interferences Table, when testing nitrate at 1 mg/L (ppm), chloride present at 76 ppm (or more) will cause a 10% (or more) positive interference. What can be done about an interfering component?

- If the interference is present below the level indicated in the User Guide, no treatment is necessary.
- If the interference is present at levels at or above the level indicated, it must be removed.
- There are Orion ISA solutions formulated to remove common interferences for selected ISEs. For example: TISAB for the fluoride ISE; blue pH-adjusting ISA for the ammonia ISE; NISS for the nitrate ISE; CISA for the chloride ISE; SAOB for the sulfide ISE.
- There are Orion ISA solutions formulated to control and remove interference due to pH. For example: TISAB; SAOB; sodium ISA; carbon dioxide ISA; ammonia ISA; cyanide alkaline reagent.
- Follow instructions in the User Guide for use of special ISAs and removal of other interferences.

What meter can I use for testing by the ISE methods described here?

- An Orion pH/ISE meter, such as a Star A214 or equivalent, can be used for testing by each method, including known addition. However, known addition on the Star A214 pH/ISE meter will require the use of a spreadsheet.
- Alternately, to automate the known addition method, use an Orion meter with incremental methods capability, such as the Orion Dual Star pH/ISE meter or the Orion Versa Star pH/ISE meter. The meter will step the user through the method, calculate, and display the final result automatically, without the use of a separate spreadsheet.

For a list of available Orion meters, ISE sensors, and solutions, visit www.thermoscientific.com/water.

Where can I find more information and assistance?

Our technical service team and local specialists are available to help. For more application notes and tips, visit the Water Analysis Instruments (WAI) Online Library at www.thermoscientific.com/waterlibrary or visit our Knowledge Base at kb.unitylabservices.com and select "Water Analysis" products.

A partial list of Orion ISE application notes available in our WAI Online Library:

- Log 126 Tip Ammonia in Seawater
- Log 35 Ammonia in Wastewater by ISE
- Log 40 Kjeldahl Nitrogen in Digested Samples
- Log 59 Calcium in Fruit Juice by ISE (Dilution Method)
- Log 15 Fluoride in Drinking Water (Direct Method)
- Log 79 Fluoride in Ocean Water by Direct Measure (Matrix Match)
- Log 16 Fluoride in Mouthwash by ISE (Direct Method)
- Log 69 Total Residual Chlorine in Wastewater by ISE
- Log 32 Sulfide in Wastewater by ISE (Direct Method)
- Log 33 Cyanide in Wastewater by ISE (Direct Method)

References

The following documents are also available in the WAI Online Library at the address noted above.

1. Application Note: Log 78 Calcium in Ocean Water by Direct Measurement (Dilution Method).
2. Application Note: Log 79 Fluoride in Ocean Water by Direct Measurement (Matrix Match Method).
3. Application Note: Log 73 Sodium in Potato Chips by Double Known Addition (DKA) Method.

thermoscientific.com/water

© 2016 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries.

Water and Lab Products

North America

Toll Free: 1-800-225-1480
Tel: 1-978-232-6000
Info.water@thermofisher.com

Germany

Tel: (49) 6184-90-6000
info.water.uk@thermofisher.com

India

Tel: (91) 22-4157-8800
wai.asia@thermofisher.com

Japan

Tel: (81) 045-453-9175
wai.asia@thermofisher.com

China

Tel: (86) 21-68654588
wai.asia@thermofisher.com

Singapore

Tel: (65) 6778-6876
wai.asia@thermofisher.com

Australia

Tel: (613) 9757-4300
in Australia (1300) 735-295
InfoWaterAU@thermofisher.com

Thermo
SCIENTIFIC

A Thermo Fisher Scientific Brand