Ion Selective Electrodes

Application Guide

Tips & Hints

Barium ISE

Day-to-Day Measurement Practice

METTLER TOLEDO

Contents

1. Introduction Ba-ISE electrode

The Barium ISE electrode is intended for measuring barium ion concentrations and activities in aqueous solutions. Its preferred applications are to be found in the field of tea, soil, water, flour etc. (Reference: A Beginners Guide to Ion-Selective Electrode Measurements – Chris C Rundle BSc, PhD)

Advantages:

- When compared to many other analytical techniques, ISE's are relatively inexpensive and simple to use and have an extremely wide range of applications and wide concentration range.
- The PVC polymer matrix membrane of Ba ISE is ideal in laboratory environments, however it has an average life-time of six months.
- Under the most favorable conditions, when measuring ions in relatively dilute aqueous solutions and where interfering ions are not a problem, they can be used very rapidly and easily (e.g. simply dipping in lakes or rivers, dangling from a bridge or dragging behind a boat).
- They are particularly useful in applications where only an order of magnitude concentration is required, or it is only necessary to know that a particular ion is below a certain concentration level.
- They are particularly useful in biological/medical applications because they measure the activity of the ion directly, rather than the concentration.
- With careful use, frequent calibration, and an awareness of the limitations, they can achieve accuracy and precision levels of ± 2-3 % for some ions and thus compare favorably with analytical techniques which require far more complex and expensive instrumentation.
- ISE's are one of the few techniques which can measure both positive and negative ions.
- They are unaffected by sample color or turbidity.
- Ba ISE's can be used in aqueous solutions over a wide temperature range up to 40 °C.

2. Basic Theory

The Ion-Selective Electrodes are part of a group of relatively simple and inexpensive analytical tools which are commonly referred to as sensors. The pH electrode is the most well-known and simplest member of this group and can be used to illustrate the basic principles of ISE's.

A barium ISE half-cell electrode measures a difference in electrical potential between itself and a reference electrode. The output potential is proportional to the amount or concentration of the barium ions present in the solution. The potential difference between the two electrodes will depend upon the activity of the barium ions in the solution. This activity represents the effective concentration of free barium ions in the solution; sample and standard solutions are brought to a constant ionic strength by adding a constant concentration of an inert electrolyte to the solutions under test in order to match the activity and concentration of a specific ion. This electrolyte is called Ionic Strength Adjustment (I.S.A.) buffer. Thus the barium ISE electrode will measure concentration directly. Activity can also be an important quantity to measure, for instance, calcium activity in blood is the physiological relevant parameter.

The measured electrode potential, E is related to the activity of barium ion by the Nernst equation.

$$E=E_o +2.303 \frac{RT}{nF} \log \text{Activity}$$

Where, E_o = a constant for a given cell

R = the gas constant

T = the temperature in Kelvin

n = the ionic charge (i.e. n = 2+)

F = the Faraday constant

and the expression $\frac{RT}{nF}$ is termed the Slope Factor

When measuring barium ions, (i.e. n =2+), the slope factor at 298 K (25 °C) has a value of 29.58 mV/pM. This is termed the Ideal Slope Factor, and means that for each tenfold change in barium concentration, an ideal measuring system will sense a mV change of 29.58 per decade.

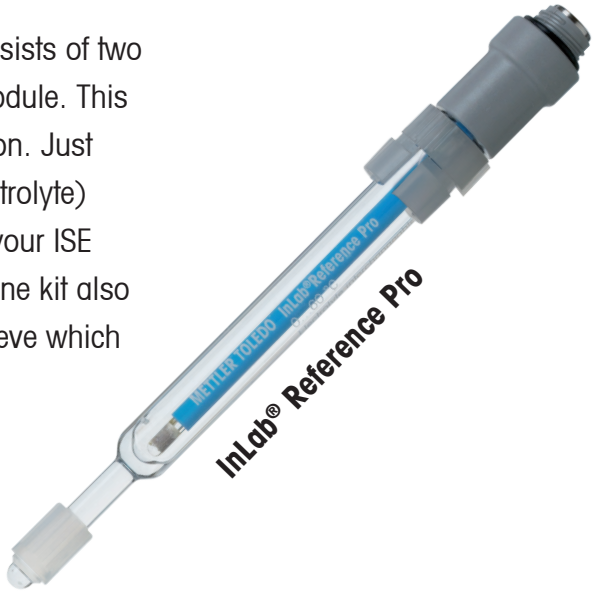
Barium ISE is a polymer PVC matrix membrane electrode. The active electrode phase is a nearly water insoluble plastic porous organophilic membrane which is in direct contact with the measurement solution. The potential measured is based on the chemical equilibrium between the Ba^{2+} ion and the complexing agent present in the membrane.

Using ISA to enhance the ionic strength, linear calibration curves of $1x10^{-5}$ mol/L are attained; the detection limit lies slightly higher than 10^{-5} mol/L. The slope, theoretically calculated from the Nernst equation to be 29.58 mV/pM at 25 °C usually lies between 27-30 mV/pM in practice.

3. Ba ISE electrodes

DX337-Ba ISE half cell electrode

METTLER TOLEDO Ion Selective Barium half-cell electrode consists of two elements: A universal shaft and an ion-specific membrane module. This module may be exchanged allowing you to measure the Ba ion. Just order the membrane kit (contents: 1 membrane, 1 vial of electrolyte) specific for that ion, mount the new module onto the shaft of your ISE half-cell, and you have a new ISE! What is more, the membrane kit also comes with an identification ring (ID ring) and an adapter sleeve which will fit any METTLER TOLEDO titration stand.

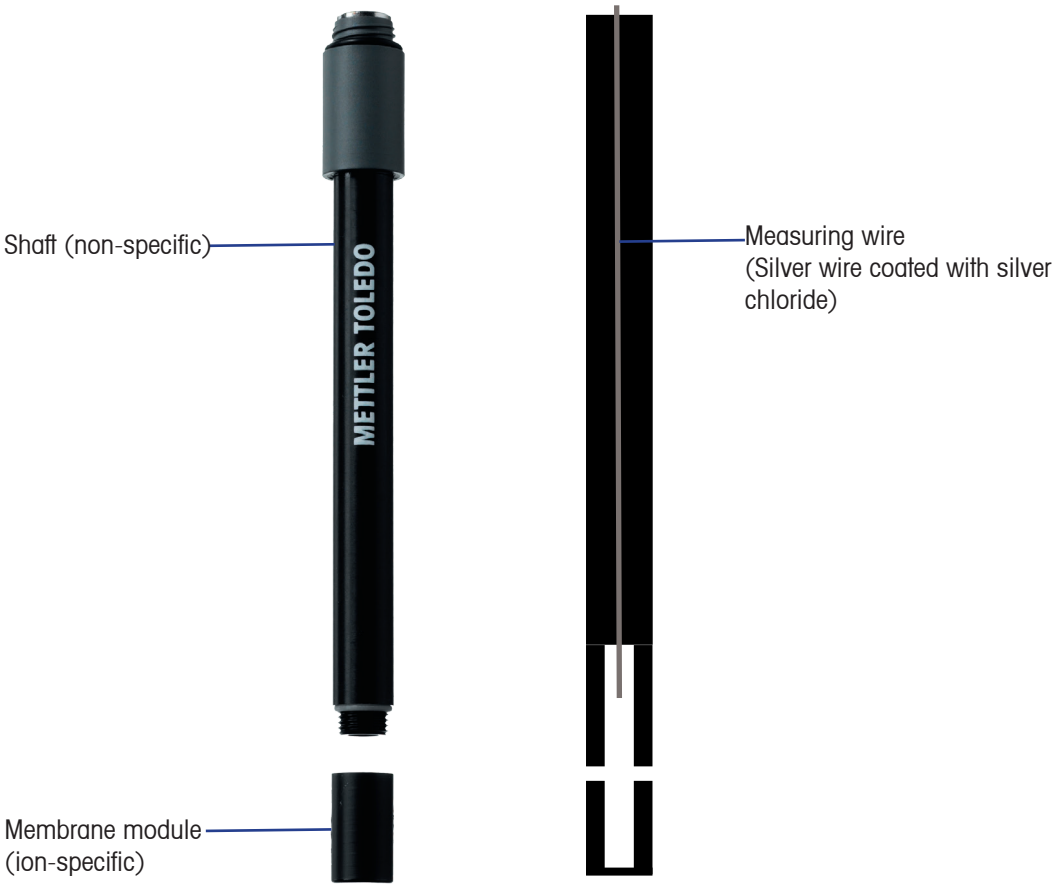


Overview of Ba-ISE electrodes	
Specification	**DX337-Ba Half Cell ISE**
Part Number	51107674 (Assembled ISE)
	51107688 (Membrane kit)
Cable	51089954 (ISE to titrator)
	52300004 (ISE to Ion meter)
Reference electrode	For Titrator - DX200 (51089935)
	For Ion meter - InLab Reference Pro (51343191)
	Cable for In Lab Reference Pro (52300016)
Membrane type	Polymer
Shaft material	POM
Reference junction	-
Reference electrolyte	-
Indicator electrolyte	51107892
ISA solution	100mM Tris2HCl
Measuring range	10^{-6} mol/L… 1 mol/L
Temperature range	0 to 40 °C
Optimal pH range	pH 2 to 12
Slope	29.58 mV/pM
Electrode resistance	Less than 10 MΩ
Response time t(99%) in conc samples close to detection limit	Several seconds to several minutes
Reproducibility	± 2 %
Interferences	Sr^{2+}, K^{+}, Na^{+}, Mg^{2+}, NH_4^{+}, Ca^{2+}, Li^{+}

4. Electrode and Measurement setup

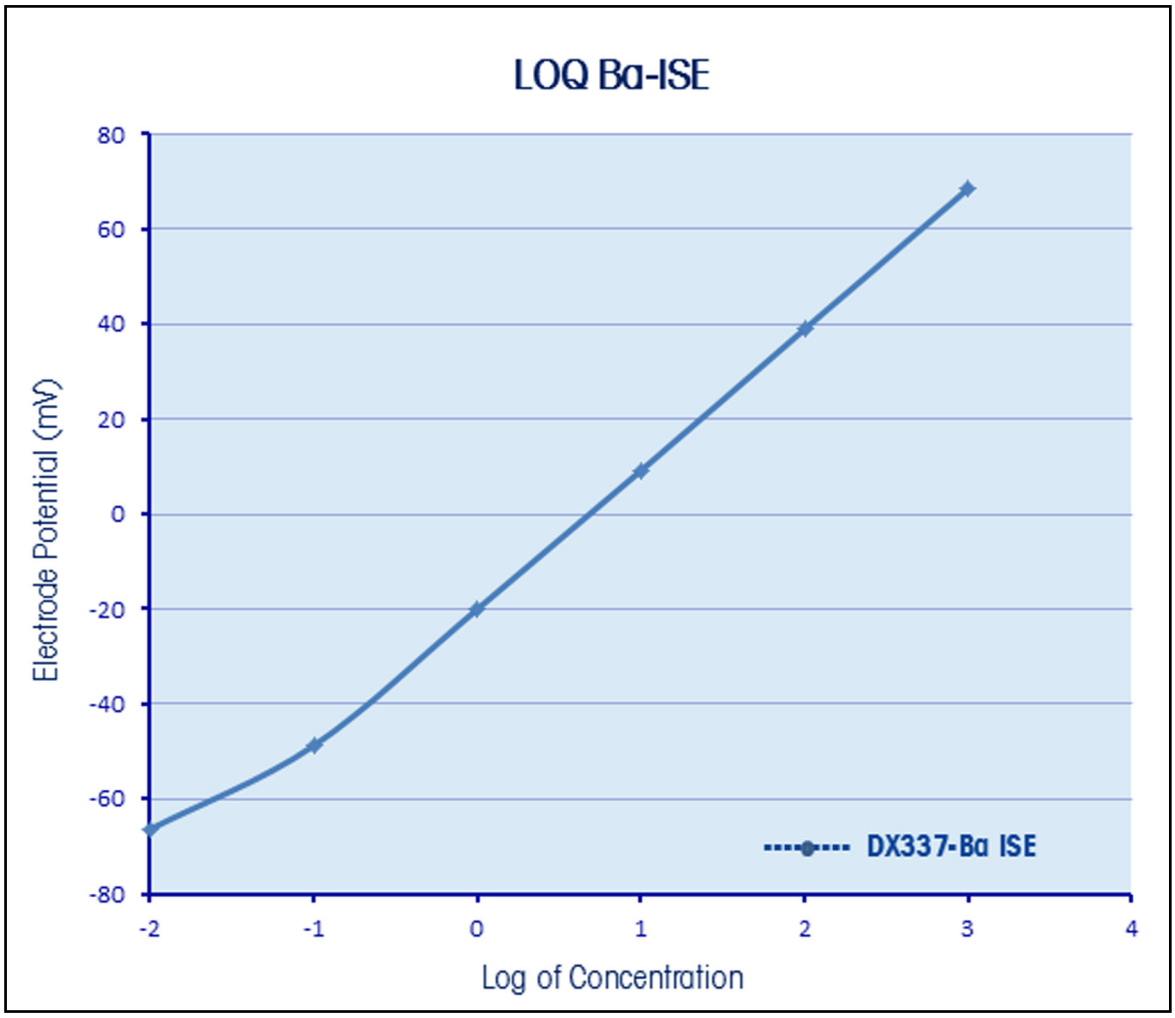
4.1 DX337-Ba ISE half-cell Electrode Preparation:

1. First withdraw the electrode from the protective tube, taking care not to touch the ion-selective membrane.
2. Remove both the black protective cap covering the electrode tip and the rubber insert covering the filling hole of the reference chamber to expose the fill hole.
3. Fill the electrode with the reference filling solution (ME-51107892) shipped with the electrode to a level just below the fill hole.
4. Prior to first usage, or after long-term storage, immerse the electrode in standard for a minimum of thirty minutes (optionally overnight).
5. Connect the electrode to the cable as recommended in the operating instructions of the meter or titrator.
6. Connect the reference electrode to the socket provided for it (4 mm banana plug for titrator and 2 mm banana plug for ion meter).



Measurement setup:

- By serial dilution of the 1000 ppm standard, prepare two or three standards whose concentration is near the expected sample concentration.
- Measure out 50 mL of each standard into individual 100 mL beakers. Add 1 mL of ISA to each standard.
- Lower the electrode tip into the more dilute solution and allow all standards and samples to come to the same temperature for precise measurements. Begin the method for calibration.
- Once the reading is over and prompts for the other standard, then rinse the electrode tip with distilled water and blot dry.
- Lower the electrode tip into the more concentrated standard solution as prompted on the terminal.
- Once the reading is over and prompts for the other standard, then rinse the electrode tip with distilled water and blot dry.
- Once the calibration gets over, check the electrode slope there should be a 27 to 30 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the Troubleshooting section.
- Add 50 mL of the sample and 1 mL of ISA into a 100 mL beaker. Lower the electrode tip into the solution. Begin the sample measurement method.
- After measurement, read the concentration directly from the titrator terminal or print the results.



- LOD is the lowest quantity of a substance that can be distinguished from the absence of that substance within a stated confidence limit.
- LOQ is the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met. The LOQ may be equivalent to the LOD or it could be at a much higher concentration.

Electrode storage:

- The half cell electrode may be stored in 100 ppm barium standard solution for short periods of time and up to three days. For longer storage more than a week, rinse and dry the membrane and cover the tip with the black rubber cap shipped with the electrode.
- The reference electrode should be drained of filling solution, and the rubber insert should be placed over the filling hole.

Ionic Strength Adjustment (ISA):

ISA provides a high and constant background ionic strength, the recommended ISA is 100 mM Tris2HCl for Half cell and other solutions can be used as long as they do not contain ions that would interfere with the electrode response to barium. Ionic activity coefficients are variable and largely depend on total ionic strength hence it is used to stabilize the barium activity coefficient by its ionic strength.

Part no.	Description
51107892	Indicator electrolyte for DX337 Ba sensor
51340045	Reference electrolyte for DX200 reference sensor

Low level ISA:

Low level ISA is a lower ionic strength adjuster with fewer components than ISA. It will enhance the electrode performance for low level measurements in samples that do not contain interfering species. Use low level ISA when measuring samples that contain less than 0.14 mg/L or 10^{-6} mol/L barium and do not contain any complexing agents.

To prepare low level ISA:

Prepare low level ISA by pipetting 25 mL of the ISA in to a 100 mL volumetric flask and dilute up to the mark with distilled water.

5. Application Tips & Hints

- All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature. Temperature should be less than 40 °C. A difference of 1 °C in temperature will result greater than 2 % measurement error.

- Constant and gentle stirring is necessary for accurate measurement.

- Always rinse the electrode tip with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover. Do not wipe or rub the sensing membrane.

- Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

- A slow or sluggish electrode response may indicate surface contamination of the membrane. If the barium electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely, hold the junction open and flush the junction with deionized water. Empty any water from the electrode and refill it with fresh filling solution. Press down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution.

- Use fresh standards for calibration.

- Re-calibrate every few hours for routine measurement.

- All samples and standards must be aqueous. They must not contain organic solvents.

- Start the calibration or measurement with the lowest concentrated standard or sample.

- Adjust the pH of the sample solutions which does not lie between the pH range of 2 to 12 before adding ISA.

6. Electrode Characteristics

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct electrode measurements reproducible to ± 2 % can be obtained. The electrode characteristics indicated are valid for DX337-Ba sensors.

Limits of Detection

In pure barium chloride solutions, the upper limit of detection is 1 mol/L. When possible, dilute the sample into the linear range of the electrode. If samples are not diluted, the possibility of a liquid reference junction potential and the salt extraction effect, need to be considered. At high salt concentrations, salts may be extracted into the electrode membrane, causing deviation from theoretical response. To measure samples between 10^{-1} and 1 mol/L, calibrate the electrode at 4 or 5 intermediate points or dilute the sample. The lower limit of detection is determined by the slight water solubility of the ion exchanger, which causes deviation from theoretical response. If barium measurements are made below 10^{-6} mol/L (0.14 mg/L as Ba^{2+}), a low-level measurement procedure is recommended.

Electrode Life

Each sensing module of Half Cell will last approximately six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that the electrode is used in. In time, there will be sluggish response or the electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to the Troubleshooting section to make sure that the difficulties are caused by the sensing module.

pH Effects

Although the electrode can be used over a wide pH range i.e. 2 to 12 pH for Half Cell, hydrogen or hydroxide ion interferes with measurements of low-levels of barium ion. The barium measurement can be made with less than 10 % error caused due to interference of hydrogen or hydroxide ion . For instance, at high pH, sufficient hydroxide ion is present to form a precipitate with a portion of barium ion. This reaction reduces level of free barium ion in the sample. Since the electrode responds only to free, unbound barium ion, it does not detect that portion of the sample barium precipitated by hydroxide ion. Precipitation can be avoided by adjusting pH of sample and standards.

Interfering ions

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water and then soaking it for a few hours a 10^{-2} mol/L or 100 mg/L barium standard. If soaking the electrode does not restore normal electrode performance, refer to the Electrode Maintenance section.

When the level of interferences in samples is constant, it is sometimes possible to measure barium accurately when interference levels are higher than those in Table below.

Interferences	Selectivity coefficient of Barium
Sr^{2+}	9.0 X 10^{-2}
K^{+}	2.0 X 10^{-2}
Na^{+}	2.0 X 10^{-2}
Mg^{2+}	6.0 X 10^{-3}
NH_4^{+}	3.0 X 10^{-3}
Ca^{2+}	2.0 X 10^{-3}
Li^{+}	2.0 X 10^{-3}

Ionic strength

The total activity of calibration and measurement solutions must be constant. By adding a constant amount of ISA solution, the background ionic strength is maintained high and constant relative to variable concentrations of barium. For barium, the recommended ISA is 100 mM Tris2HCl for Half cell ISE's. Other solutions can be used as long as they do not contain ions that would interfere with the electrode response to barium.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 °C of each other. At the 10^{-3} mol/L level, a 1 °C difference in temperature results in 1.2 % error. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the barium electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Theoretical values of the Nernst equation for barium ion are given in Table below. If the temperature changes occur, meter and electrode should be recalibrated. The electrode can be used at temperatures from 0-40 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, equilibrium time of up to one hour is recommended.
The isopotential point is the concentration at which the potential of the electrode does not vary with temperature. Since the isopotential point of this electrode is known, the combination of barium electrode may be used on meters that allow automatic temperature compensation for ISE measurements. By programming in the isopotential point and placing an ATC probe into the sample, any time the temperature changes the meter will automatically adjust the slope of the calibration curve, resulting in more accurate measurements.
Values of theoretical electrode slope Vs temperature is explained below.

Temp (°C)	Slope (mV/pM)
0	27.1
10	28.1
20	29.1
25	29.6
30	30.1
40	31.1

Bridging electrolyte

As bridging electrolyte for the reference electrode, a 3 mol/L KCl solution is used with the sensor.

Conditioning

For the determination of concentrations under 0.1 mg/L, the electrode should be conditioned in Low Level ISA solution for approx. 30 minutes.

Storage

Store electrodes between measurements and up to three days, in a 10^{-2} mol/L or 100 mg/L barium standard, the filling solution inside the electrode should not be allowed to evaporate. For storage longer than one week, drain the electrode, flush the chamber with distilled water and store the sensing module in the glass vial.

Handling

Do not wipe or rub the electrode sensing element. Check the electrode sensing surface for air bubbles and remove air bubbles by re-immersing the electrode in the solution and gently tapping it. Avoid deposits on the polymer membrane; do not touch with bare fingers.

Complexation and precipitation

The electrode responds to the free barium ions in solution, and not to barium which is bound or complexed. Certain barium compounds are relatively insoluble. Among them, in the order of least soluble first, are barium chlorate, nitrates, hydroxide and carbonate.

Barium forms soluble complexes with certain inorganic species, such as hydroxide, carbonate, nitrate, chlorate, phosphates and ammonia. It also forms complexes with organic anions, such as tartrate, EDTA. The extent of complexation increases with in¬creasing barium concentration and more alkaline pH, and will vary with the sample ionic strength.

7 Troubleshooting

- No reference filling solution added:
  Fill the electrode with filling solution up to the fill hole. Refer to the Electrode preparation section of the electrode guidebook.

- Incorrect reference filling solution used:
  Refer to the Electrode Preparation section of the electrode guidebook to verify the correct electrode filling solution.

- Electrode junction is dry:
  Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

- Electrode is clogged or dirty:
  Refer to the Electrode Maintenance section for cleaning instructions of the electrode guidebook

- Standards are contaminated or made incorrectly:
  Prepare fresh standards.

- ISA not used or incorrect ISA used:
  ISA must be added to all standards and samples.

- Samples and standards at different temperatures:
  Allow solutions to reach the same temperature.

- Air bubble on sensing element:
  Remove air bubble by re-immersing the electrode in solution.

- Electrode not properly connected to meter:
  Unplug and reconnect the electrode to the meter.

- Meter/Titrator or stir plate not properly grounded:
  Check the meter/titrator and stir plate for proper grounding.

- Static electricity present:
  Wipe plastic parts on the meter/titrator with a detergent solution.

- Defective meter/titrator:
  Check the meter/titrator performance. See the meter/titrator user guide.

8. Selected Applications

Calibration of Ba-ISE electrodes

In this method the Barium ISE electrodes are calibrated using several Barium standard solutions

Sample	Barium standard solutions (50 mL) 0.1 ppm, 1 ppm, 10 ppm, 100 ppm, 1000 ppm
Compound	Barium, Ba M = 137.3, z = 1
Chemicals	Reference electrolyte for DX200 (ME-51340045) Electrolyte for Half Cell (ME-51107892) ISA 100 mM Tris2HCl
Titrant	-
Standard	-
Indication	DX337-Ba ISE + DX200 Ref. Electrode
Chemistry	-
Calculation	R1 = E (mV) Potential measurement of the standard solutions
Waste disposal	-
Author, Version	Shrikant Sawant, IMSG AnaChem, Version 1.0 Revised: C. De Caro, MSG AnaChem

Preparation and Procedures

CAUTION

- Use safety goggles, a lab coat and wear gloves. If possible, work in a fume hood.
- Ensure accurate cleaning of sensor is sufficient after each titration.
- The required barium standard solutions are prepared by serial dilution of the 1000 ppm standard solution.
- The barium solutions are defined as a list of standards "Barium ppm".
- Three titration beakers are filled with 50 mL of each barium solutions i.e. 0.1 ppm, 1 ppm and 10 ppm.
- 1 mL ISA solution is added with a pipette to each beaker.
- Connect the first beaker to the titration stand and start the method.
- After measurement of each solution the electrodes are cleaned with deionized water before starting the next sample.

Remarks

- The calibration data are automatically stored in the setup data of the titrator. They are assigned to the sensor used in the method and are only valid for this sensor.
- Calibration and measurement solutions should be always at the same temperature.
- Rinse electrode with deionized water after each measurement and remove adhering water drops with a soft paper tissue.
- Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.
- Check a slow or sluggish electrode response, empty the electrode completely, hold the junction open and flush the junction with distilled water.

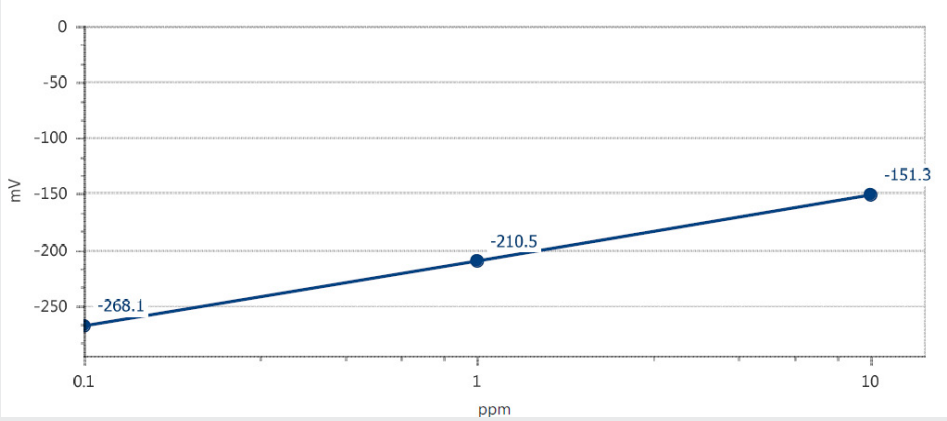
Instruments	- Titration Excellence T50/T70/T90 (Other Titrators: depending on instrument type, manual operation and method changes are necessary) - Seven Excellence Ion meter
Accessories	- PP Titration beakers (ME-51109388) - Rainin pipette - DT1000 Temperature sensor (ME-51109828)

Results

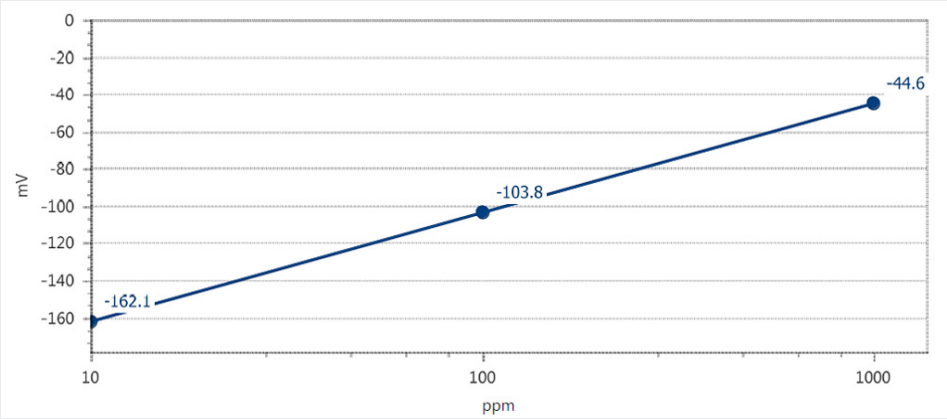
Results for Segmented Calibration of Ba-ISE electrodes			
DX337-Ba ISE (1)			
Standard (ppm)	**Measured values (mV)**	**Zero point (pM)**	**Slope (mV/pM)**
0.1	-48.7	-0.684	-28.82
1	-19.7		
10	9.1	-0.681	-28.93
DX337-Ba ISE (2)			
Standard (ppm)	**Measured values (mV)**	**Zero point (pM)**	**Slope (mV/pM)**
0.1	-48.4	-0.597	-29.82
1	-17.8		
10	12.0	-0.583	-30.54

Results for Segmented Calibration of Ba-ISE electrodes			
DX337-Ba ISE (1)			
Standard (ppm)	**Measured values (mV)**	**Zero point (pM)**	**Slope (mV/pM)**
10	10.3	-0.641	-29.50
100	40.1		
1000	69.6	-0.655	-29.81
DX337-Ba ISE (2)			
Standard (ppm)	**Measured values (mV)**	**Zero point (pM)**	**Slope (mV/pM)**
10	10.1	-0.650	-28.52
100	38.5		
1000	67.0	-0.645	-28.40

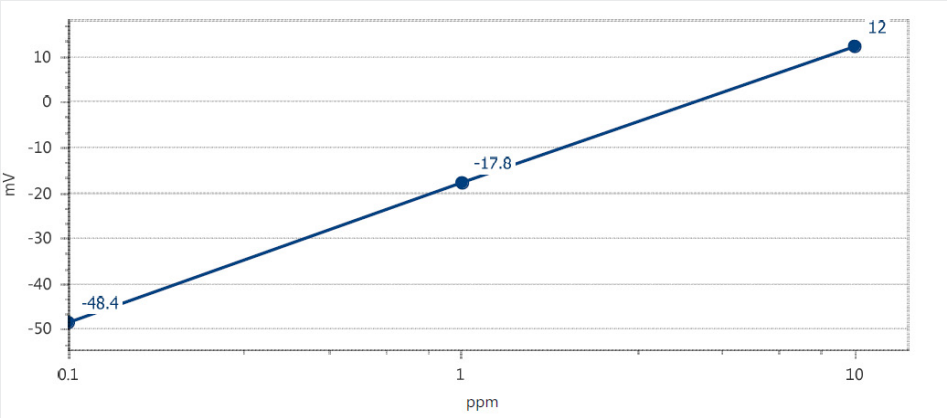
Titration curve



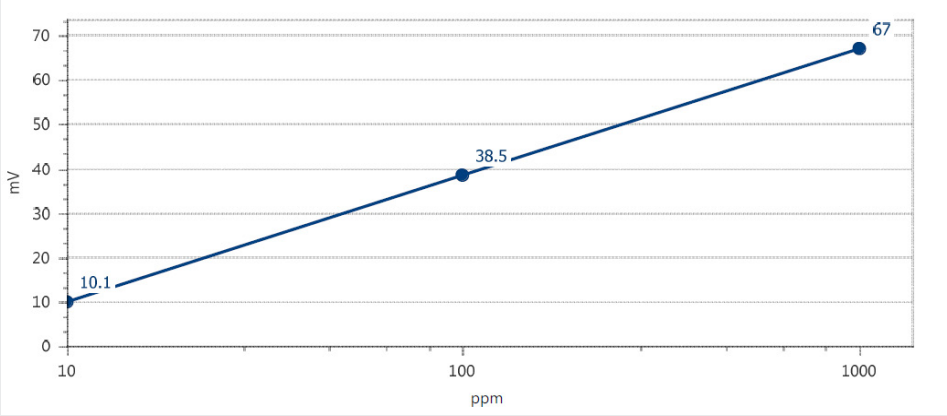
Calibration of DX337-Ba ISE (1) [0.1, 1, 10 ppm std]



Calibration of DX337-Ba ISE (1) [10, 100, 1000 ppm std]



Calibration of DX337-Ba ISE (2) [0.1, 1, 10 ppm std]



Calibration of DX337-Ba ISE (2) [10, 100, 1000 ppm std]

Comments

- Use fresh standards for calibration.
- Re-calibrate every few hours for routine measurement.
- All samples and standards must be aqueous. They must not contain organic solvents.

Results of pH/Ion meter Calibration:

Results for Calibration of Ba-ISE electrodes with Seven Excellence pH/Ion meter							
DX337 Ba-ISE							
Standard (ppm)	**Measured values (mV)**	**Offset (mV)**	**Slope (mV/pM)**	**Standard (ppm)**	**Measured values (mV)**	**Offset (mV)**	**Slope (mV/pM)**
0.1	-48.4	125.5	-29.04	10	32.4	151.3	-30.19
1	-19.3			100	61.8		
10	9.7	122.5	-28.43	1000	91.6	149.9	-29.73

Method

001 Title

Type	General titration
Compatible with	T50 / T70 / T90
ID	Cal_HalfCell_Ba_03
Title	
. . .	

002 Sample (Calib.)

Sensor

Sensor Type	ISE
Sensor	DX337-Ba^{2+}
Ion Charge	2
Unit	ppm

Calibration

List of standards	DX337-Ba^{2+}
Calibration	Segmented
Number of standards	3
Standard 1	0.1
Standard 2	1.0
Standard 3	10.0

Temperature

Temperature	25.0 °C

003 Titration stand (Manual stand)

Type	Manual stand
Titration stand	Manual stand 1

004 Stir

Speed	30 %
Duration	180 s
Condition	No

005 Measure (normal) [1]

Sensor

Type	ISE
Sensor	DX337-Ba^{2+}
Unit	mV
Ion charge	2

Temperature acquisition

Temperature acquisition	Yes
Temperature sensor	DT1000
Temperature unit	°C

Stir

Speed	30 %

Acquisition of measured values

Acquisition	Equilibrium controlled
dE	0.5 mV
dt	1 s
t (min)	3 s
t (max)	30 s
Mean value	No

Condition

Condition	No

006 Calibration

Calibration

Sensor	DX337-Ba^{2+}
Limits	No
Condition	No

007 End of sample

008 Record

Report

Report template	Calibration report
Print	No
Condition	No

Seven Excellence pH/Ion meter Method

Title

Method type	Calibration
Method ID	CALBARIUM
Title	Calibration
. . . .	

Configuration

Measurement type	Ion
Sensor name	MTIonSensor
Temperature capture	Manual

Sample (Calibration)

Measurement type	Ion
Sensor name	MTIonSensor
Calibration standard	Mettler Toledo Ion (Ref25 °C) Group
Unit	mg/L
Calibration mode	Segmented
Number of standards	3
Standard 1	0.1
Standard 2	1
Standard 3	10
Temperature	25.0 °C
Comment	--

Measure (Calibration)

Sensor name	MTIonSensor
Endpoint type	Automatic
Endpoint criteria	Standard
Stir	Yes
Stirring speed	30%

Report

Print	No

Barium Determination with Barium Ion Selective Electrode

Barium content determination in aqueous standard solution by means of Barium ISE electrodes.

Sample	Barium standard solutions (50 mL) Barium Chloride, BaCl2, M=244.28
Compound	Barium, Ba M = 137.3, z = 1
Chemicals	Reference electrolyte for DX200 (ME-51340045) Electrolyte for Half Cell (ME-51107892) ISA-100 mM Tris2HCl
Titrant	-
Standard	-
Indication	DX337-Ba ISE + DX200 Ref. Electrode
Chemistry	-
Calculation	R1 = E (ppm)
Waste disposal	-
Author, Version	Shrikant Sawant, IMSG AnaChem, Version 1.0 Revised: C. De Caro, MSG AnaChem

Preparation and Procedures

CAUTION

- Use safety goggles, a lab coat and wear gloves. If possible, work in a fume hood.
- Ensure accurate cleaning of sensor is sufficient after each titration.

1. The required barium standard solutions are prepared.
2. The Ba ISE is previously adjusted (calibrated) using barium chloride standard solutions (see application M265).
3. The titration beakers are filled with 50 mL standard solution.
4. 1 mL ISA solutions are added with a pipette to each beaker.
5. Connect the first beaker to the titration stand and start the method.
6. After measurement of each solution the electrodes are cleaned with deionized water before starting the next sample.

Remarks

1. To improve accuracy and reproducibility of the measurement, perform the electrode calibration and sample measurement at the same temperature and stirring speed.
2. The titrator corrects the slope of the sensor according to the Nernst equation by manual entry or temperature measurement with a temperature sensor.
3. Rinse electrode with deionized water after each measurement and remove adhering water drops with a soft paper tissue.

Instruments	- Titration Excellence T50/T70/T90 (Other Titrators: depending on instrument type, manual operation and method changes are necessary)
Accessories	- PP Titration beakers (ME-51109388) - Rainin pipette - DT1000 Temperature sensor (ME-51109828)

Results

Concentration (ppm)	DX337-Ba ISE (1)		DX337-Ba ISE (2)	
	Mean Recovery (ppm)	RSD (%) of 6 Replicates	Mean Recovery (ppm)	RSD (%) of 6 Replicates
0.7	0.699	0.704	0.702	0.799
6	5.993	0.301	5.998	0.186
60	59.831	0.097	59.809	0.144
550	548.371	0.094	548.640	0.253

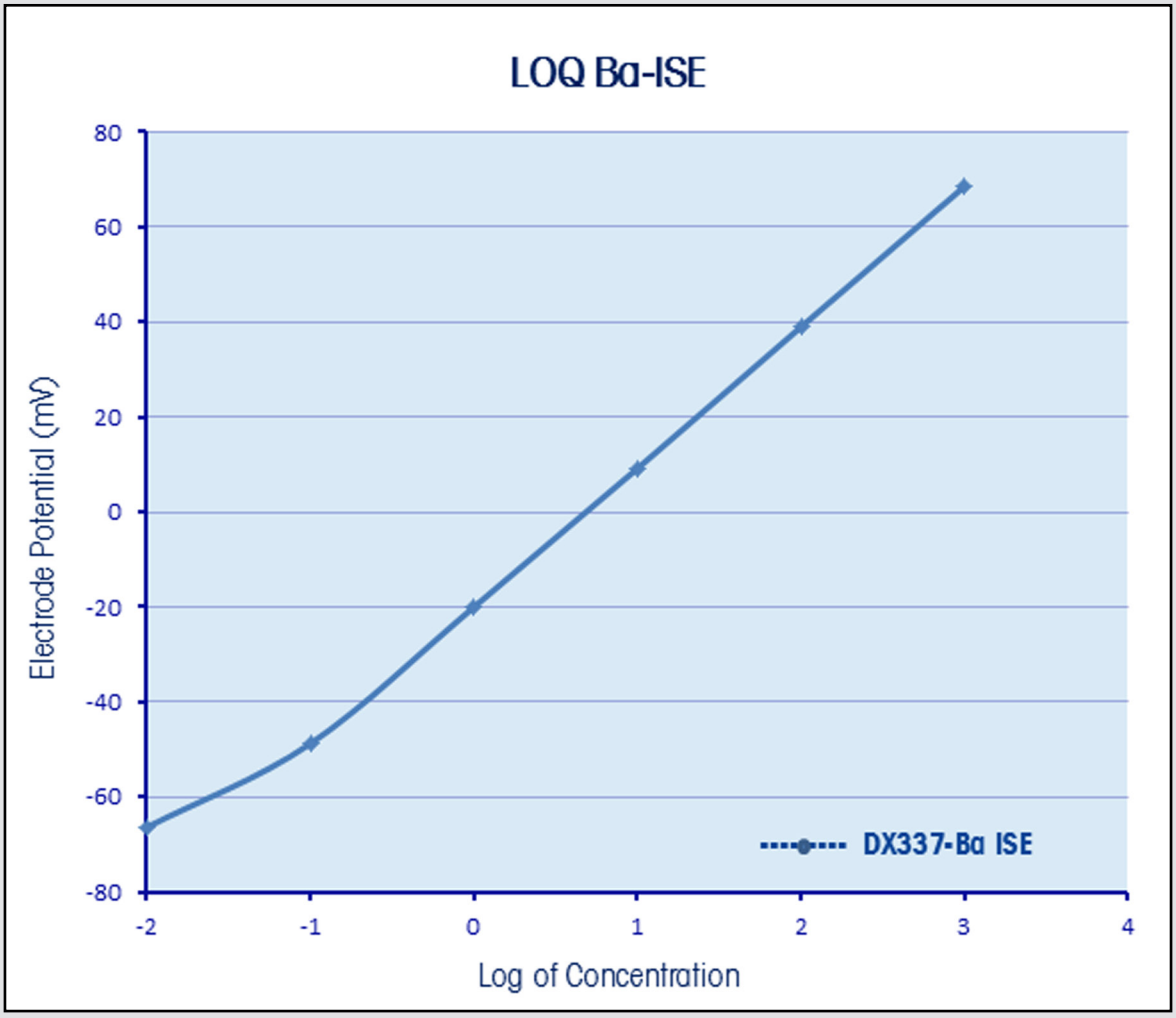
Method-A Measures once after a stir time of 180 s. The barium concentration is calculated from this. If the sample is diluted for the measurement, the dilution factor can be entered as a correction factor (f) for each sample. This will be used in the calculation.

Method-B Stir for 180 s then takes 6 measurements at an interval of 1-2 seconds. The barium concentration is calculated from the mean of these 6 measured values.

Method – A				
Concentration (ppm)	DX337-Ba ISE (1)		DX337-Ba ISE (2)	
	Mean Recovery (ppm)	RSD (%) of 6 Replicates	Mean Recovery (ppm)	RSD (%) of 6 Replicates
0.7	0.699	0.704	0.702	0.799
6	5.993	0.301	5.998	0.186
60	59.831	0.097	59.809	0.144
550	548.371	0.094	548.640	0.253
Method - B				
Concentration (ppm)	DX337-Ba ISE (1)		DX337-Ba ISE (2)	
	Mean Recovery (ppm)	RSD (%) of 6 Replicates	Mean Recovery (ppm)	RSD (%) of 6 Replicates
0.7	0.699	0.839	0.701	0.583
6	6.002	0.334	5.986	0.215
60	59.935	0.304	59.967	0.286
550	548.336	0.149	549.020	0.079

Comments

The concentration ppm leaves the linear range (see the below graph). The range of concentrations for Nitrate ISE was therefore limited to 0.1 ppm → limit of quantification.



Method

Method - A

001 Title

Type	General titration
Compatible with	T50 / T70 / T90
ID	M1_Ba_SPL_01
Title	___
. . .	

002 Sample

Number of IDs	1
ID 1	Sample 50.0
Entry type	Fixed volume
Volume	50 mL
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0 °C

003 Titration stand (Manual stand)

Type	Manual stand
Titration stand	Manual stand 1

004 Stir

Speed	30 %
Duration	180 s
Condition	No

005 Measure (normal) [1]

Sensor

Type	ISE
Sensor	DX337-Ba^{2+}
Unit	ppm

Temperature acquisition

Temperature acquisition	Yes
Temperature sensor	DT1000
Temperature unit	°C

Stir

Speed	30 %

Acquisition of measured values

Acquisition	Equilibrium controlled
dE	0.5 mV
dt	1 s
t (min)	3 s
t (max)	30 s
Mean value	No

Condition

Condition	No

006 Calculation R1

Result	Content
Result unit	ppm
Formula	R1=E
Constant	C=1
M	M[None]
z	z[None]
Decimal places	3
Result limits	No
Extra statistical func.	No
Send to buffer	No
Condition	No

007 End of sample

008 Record

Report

Report template	Titration report_01
Print	No
Condition	No

Method - B

001 Title

Type	General titration
Compatible with	T50 / T70 / T90
ID	M1_Ba_SPL_03
Title	___
. . .	

002 Sample

Number of IDs	1
ID 1	Sample 50.0
Entry type	Fixed volume
Volume	50 mL
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0 °C

003 Titration stand (Manual stand)

Type	Manual stand
Titration stand	Manual stand 1

004 Stir

Speed	30 %
Duration	180 s
Condition	No

005 Measure (normal) [1]

Sensor

Type	ISE
Sensor	DX337-Ba^{2+}
Unit	ppm

Temperature acquisition

Temperature acquisition	Yes
Temperature sensor	DT1000
Temperature unit	°C

Stir

Speed	30 %

Acquisition of measured values

Acquisition	Equilibrium controlled
dE	0.5 mV
dt	1 s
t (min)	3 s
t (max)	30 s
Mean value	Yes
No. of measured value	6
dt (s)	1

Condition

Condition	No

006 Calculation R1

Result	Content
Result unit	ppm
Formula	R1=E
Constant	C=1
M	M[None]
z	z[None]
Decimal places	4
Result limits	No
Extra statistical func.	No
Send to buffer	No
Condition	No

007 End of sample

008 Record

Report

Report template	Titration report_01
Print	No
Condition	No

Barium determination in samples

Barium content determination in selected samples by direct measurement with Barium ISE electrodes.

Sample	Barium sample solutions (50 mL) Barium chloride, BaCl2, M = 244.28
Compound	Barium, Ba M = 137.3, z = 1
Chemicals	Reference electrolyte for DX200 (ME-51340045) Electrolyte for Half Cell (ME-51107892) ISA-100 mM Tris2HCl
Titrant	-
Standard	-
Indication	DX337-Ba ISE + DX200 Ref. Electrode.
Chemistry	-
Calculation	R1 = E (ppm) R2 = R1*f (ppm)/(µg/g) f = Dilution factor
Waste disposal	-
Author, Version	Shrikant Sawant, IMSG AnaChem, Version 1.0 Revised: C. De Caro, MSG AnaChem

Preparation and Procedures

CAUTION

- Use safety glasses, a lab coat and wear gloves. If possible, work in a fume hood.
- Ensure accurate cleaning of sensor is sufficient after each titration.

Sample handling

- The Ba ISE electrode is previously adjusted (calibrated) using barium chloride standard solutions (see application M665)
- The required amount of sample is taken into the titration beaker. Details of sample preparation are given under comments section.
- 1 mL ISA solutions are added with a pipette to each beaker.
- Connect the first beaker to the titration stand and start the method.
- After measurement of each solution the electrodes are cleaned with deionized water before starting the next sample.

Remarks

- To improve accuracy and reproducibility of the measurement, perform the electrode calibration and sample measurement at the same temperature and stirring speed.
- The titrator corrects the slope of the sensor according to the Nernst equation by manual entry or temperature measurement with a temperature sensor.
- Rinse electrode with deionized water after each measurement and remove adhering water drops with a soft paper tissue.
- For the sample which has concentration below 0.1 ppm of barium discard atleast first three sample measurement

Instruments	- Titration Excellence T50/T70/T90 (Other Titrators: depending on instrument type, manual operation and method changes are necessary) - Seven Excellence Ion meter
Accessories	- PP Titration beakers (ME-51109388) - Rainin pipette - DT1000 Temperature sensor (ME-51109828)

Results

Instruments	Samples	Label Claim (ppm)/(µg/g)	DX337 Ba ISE	
			Mean Result of 6 Samples (ppm)/(µg/g)	RSD (%)
T90/T70/T50	Potable water	- NA -	3.536	0.207
	Tap water	- NA -	4.336	0.538
	River water	- NA -	1.922	0.427
	Sea water	- NA -	2.406	0.291
	Industrial waste	- NA -	274.730	0.279
	Tea	- NA -	8.872	0.405
	Soil	- NA -	6.718	0.982
	Wheat flour	- NA -	3.636	0.809
	Raspberries	- NA -	0.131	0.786
	Strawberry	- NA -	0.150	0.843
Seven Excellence Ion meter	Potable water	- NA -	3.600	0.000
	Tap water	- NA -	4.400	0.000
	River water	- NA -	1.800	0.000
	Sea water	- NA -	2.500	0.000
	Industrial waste	- NA -	274.833	0.088
	Tea	- NA -	8.961	0.333
	Soil	- NA -	7.023	0.342
	Wheat flour	- NA -	3.950	0.300
	Raspberries	- NA -	0.994	0.203
	Strawberry	- NA -	1.986	0.138

Results

No.	Strawberry Sample Weight	DX337 Ba ISE	Tea Sample Weight	DX337 Ba ISE
1	5.0008 g	R1= 0.149 ppm	2.1100 g	R1= 0.375 ppm
		R2= 1.490 µg/g		R2= 8.886 µg/g
2	5.0005 g	R1= 0.148 ppm	2.1093 g	R1= 0.376 ppm
		R2= 1.480 µg/g		R2= 8.913 µg/g
3	5.0001 g	R1= 0.151 ppm	2.1156 g	R1= 0.376 ppm
		R2= 1.510 µg/g		R2= 8.886 µg/g
4	5.0007 g	R1= 0.151 ppm	2.1178 g	R1= 0.373 ppm
		R2= 1.510 µg/g		R2= 8.806 µg/g
5	5.0011 g	R1= 0.151 ppm	2.1145 g	R1= 0.375 ppm
		R2= 1.510 µg/g		R2= 8.867 µg/g
6	5.0006 g	R1= 0.150 ppm	2.1181 g	R1= 0.376 ppm
		R2= 1.500 µg/g		R2= 8.876 µg/g
	Mean	R1= 0.150 ppm	Mean	R1= 0.375 ppm
		R2= 1.500 µg/g		R2= 8.872 µg/g
	Rel. standard deviation	0.843 %	Rel. standard deviation	0.312 %
		0.843 %		0.405 %

Automation is not used for ISE measurement due to clinging water drops on the electrode and stirrer after rinsing. This leads to erroneous results by lowering the sample concentration.

Comments

Sample	Preparation
Potable water	Take 50 mL of Potable water into a clean titration beaker add 1.0 mL of ISA solution stir the solution to mix for few minutes and measure.
Tap water	Take 50 mL of Tap water into a clean titration beaker add 1.0 mL of ISA solution stir the solution to mix for few minutes and measure.
River water	Take 50 mL of River water into a clean titration beaker add 1.0 mL of ISA solution stir the solution to mix for few minutes and measure.
Sea water	Take 50 mL of Sea water into a clean titration beaker add 1.0 mL of ISA solution stir the solution to mix for few minutes and measure.
Industrial water	Take 50 mL of Industrial water into a clean titration beaker add 1.0 mL of ISA solution stir the solution to mix for few minutes and measure.
Tea	Carefully weigh 2.0 grams of Tea into a clean titration beaker add 50 mL of deionized water and 1.0 mL of ISA solution, stir the solution to homogenize and measure.
Soil	Carefully weigh 2.0 grams of Soil into a clean titration beaker add 50 mL of deionized water and 1.0 mL of ISA solution, stir the solution to homogenize and measure.
Wheat flour	Carefully weigh 2.5 grams of Wheat flour into a clean titration beaker add 50 mL of deionized water and 1.0 mL of ISA solution, stir the solution to homogenize and measure.
Raspberries	Carefully cut the raspberries into small pieces weigh 5.0 grams of sample into a clean titration beaker add 50 mL of deionized water and 1.0 mL of ISA solution, stir the solution to homogenize and measure.
Strawberry	Carefully cut the strawberries into small pieces weigh 5.0 grams of sample into a clean titration beaker add 50 mL of deionized water and 1.0 mL of ISA solution, stir the solution to homogenize and measure.

Remarks:

The calibration and barium concentration determination of each sample is automatically performed in a method. Between the calibration and measurement, the electrode is conditioned for 5 minutes in deionized water to prevent contamination with barium ions.

Method

001 Title

Type	General titration
Compatible with	T50 / T70 / T90
ID	M1_Ba_SPL_05
Title	___
. . .	

002 Sample

Number of IDs	1
ID 1	Sample
Entry type	Weight
Lower limit	0.0 g
Upper limit	10.0 g
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0 °C
Entry	Arbitrary

003 Titration stand (Manual stand)

Type	Manual stand
Titration stand	Manual stand 1

004 Stir

Speed	60 %
Duration	10 s
Condition	No

005 Measure (normal) [1]

Sensor

Type	ISE
Sensor	DX337-Ba^{2+}
Unit	ppm
Ion charge	2

Temperature acquisition

Temperature acquisition	Yes
Temperature sensor	DT1000
Temperature unit	°C

Stir

Speed	30 %

Acquisition of measured values

Acquisition	Equilibrium controlled
dE	0.5 mV
dt	1 s
t (min)	3 s
t (max)	30 s
Mean value	No

Condition

Condition	No

006 Calculation R1

Result	Content
Result unit	ppm
Formula	R1=E
Constant	C=1
M	M[None]
z	z[None]
Decimal places	4
Result limits	No
Extra statistical func.	No
Send to buffer	No
Condition	No

007 Calculation R2

Result	Content
Result unit	µg/g
Formula	R2=R1*f/m
Constant	C=1
M	M[None]
z	z[None]
Decimal places	3
Result limits	No
Extra statistical func.	No
Send to buffer	No
Condition	No

008 End of sample

009 Record

Report

Report template	Titration report_01
Print	No
Condition	No

001 Title

Type	General titration
Compatible with	T50 / T70 / T90
ID	M1_Ba_SPL_05
Title	___
. . .	

002 Sample

Number of IDs	1
ID 1	Sample 50.0
Entry type	Fixed volume
Volume	50.0 mL
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0 °C

003 Titration stand (Manual stand)

Type	Manual stand
Titration stand	Manual stand 1

004 Stir

Speed	60 %
Duration	10 s
Condition	No

005 Measure (normal) [1]

Sensor

Type	ISE
Sensor	DX337-Ba^{2+}
Unit	ppm
Ion charge	2

Temperature acquisition

Temperature acquisition	Yes
Temperature sensor	DT1000
Temperature unit	°C

Stir

Speed	30 %

Acquisition of measured values

Acquisition	Equilibrium controlled
dE	0.5 mV
dt	1 s
t (min)	3 s
t (max)	30 s
Mean value	No

Condition

Condition	No

006 Calculation R1

Result	Content
Result unit	ppm
Formula	R1=E
Constant	C=1
M	M[None]
z	z[None]
Decimal places	4
Result limits	No
Extra statistical func.	No
Send to buffer	No
Condition	No

007 End of sample

008 Record

Report

Report template	Titration report_01
Print	No
Condition	No

9. References

- " Direct Measurements with Ion Selective Electrodes", METTLER TOLEDO Titration Applications Brochure No. 6, ME-51724646
- "A Guide to Ion Selective Measurement", METTLER TOLEDO, ME-51300075

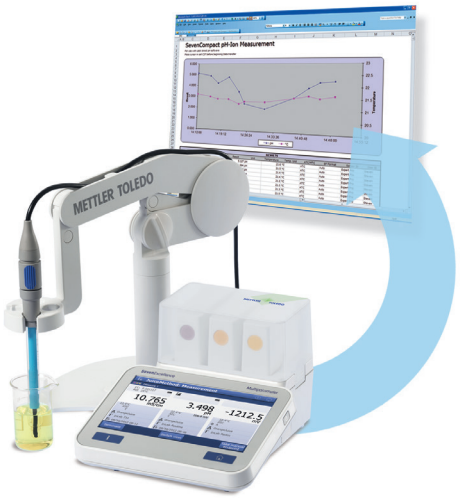
This application bulletin represents selected, possible application examples. These have been tested with all possible care in our lab with the analytical instrument mentioned in the bulletin. The experiments were conducted and the resulting data evaluated based on our current state of knowledge.
However, the application bulletin does not absolve you from personally testing its suitability for your intended methods, instruments and purposes. As the use and transfer of an application example are beyond our control, we cannot accept responsibility therefore.

When chemicals and solvents are used, the general safety rules and the directions of the producer must be observed

Application Guide Ion Selective Electrode - Barium

All METTLER TOLEDO methods (including procedures, literature references and results) are shown and described in detail. The methods are a collection of representative barium analysis.

Enjoy an extremely easy and efficient method development in all models of the Titration Excellence line and Seven Excellence pH/Ion meter.



Seven Excellence pH/Ion meter

Titration Excellence

www.mt.com

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