pH Measurement

Meter Selection
Sensor Selection
Ideal Equipment
Temperature
Tricky Cases
System Check
Maintenance

pH Workflow Optimization
in 7 Steps

METTLER TOLEDO

Editorial

Dear Reader,

The pH value is determined in a huge variety of samples in almost any chemical, biological, agricultural, alimentary or medical lab. The pH result serves as one of the most important indicators of the general quality of raw material as well as intermediate or final products. In food and beverages it even has an immediate effect on the customer experience; in case of medication on the effectiveness.

Often, the determination of pH is just one step in a whole lab workflow, similar to weighing. pH results must be attained quickly and easily as not to slow down the everyday tasks. By following these 7 steps a pH reading is taken rapidly, not taking more than a few minutes, sometimes less than 1 minute.

METTLER TOLEDO

Content

1 Select the Meter that Matches Your Needs

1.1 Does your pH meter meet your needs?

By following a few simple rules and, of course, selecting the right equipment, you can achieve highly accurate results.

Figure 1: Example of a routine meter:
SevenCompact™, for routine tasks that require precision.

Figure 2: Example of an advanced meter:
SevenExcellence™, for regulated labs and automation.

The right meter

Maximize accuracy and precision by choosing a meter that:
- has the appropriate error limits and measuring range for your applications
- allows a broad enough range of calibration points and calibration algorithms
- offers the correct level of security through user management, password protection etc.
- supports your compliance and automation needs.

1.2 Typical requirements and solutions – pH meters

Users of pH meters have many different needs and requirements to cover. Therefore, manufacturers offer a variety of meters to match. The range starts at rather simple meters with few functionalities and ends at high performance meters with a lot of functionalities regarding ease of use, compliance and automation.

	Typical Requirements	**Typical Solutions**
Professional Performance Level	Touch screen	One Click™ operation
	Easy to read display	Large color display
	Extended memory	Memory for methods and analysis incl. statistics
	Data export functions	Export to USB stick, network printer and RS232 printer
	Enhanced compliance with regulations – User management – Calibration procedure – Internal clock	 4 user-levels Calibration reminder, free buffers Radio controlled automatic clock
	ISM functionalities[1]	Full
	Ingress protection	IP54[2]
	Automation option	Sample changer, stirrer, LabX software
Routine Performance Level	Modern display	Color display
	Extended memory	Data memory
	Data export functions	Export to USB stick and RS232 printer
	Enhanced compliance with regulations – User management – Calibration procedure – Internal clock	 Routine and expert mode Calibration reminder, set of buffers Set data and time
	ISM functionalities[1]	Full
	Ingress protection	IP54[2]
Entry Performance Level	Clear display	LCD display for measured values and temperature
	Simple operation	Keypad with few keys only
	Medium resolution	0.1 pH, 1 mV
	Calibration procedure support	Max. 3 point calibration, 4 Sets of predefined buffers
	Ingress protection	IP54[2]

Table 1: Typical requirements and solutions for pH meters.

[1] ISM: Intelligent Sensor Manegement. Relevant sensor data (name, S/N, calibration data) are automatically added to the meter upon connection of the sensor.
[2] IP 54 means dust-proof as well as water-resistant to water sprayed from all directions. Limited ingress is permitted.

2 Choose the Best Suited Sensor

Who does not know this: the pH sensor gets sluggish within weeks, the junction looks dirty, and the membrane or the plastic shaft is damaged. What happened? Answer: The wrong pH electrode is in use! Not enough attention was paid to the selection of the pH sensor: one of the most common mistakes when setting up a lab or when choosing the lab equipment.

A lot of trouble can be avoided by getting some advice on the sensor selection, ideally first from www.mt.com/electrode-guide. Once you have found the best suited electrode, maintenance is reduced to a minimum, the lifetime of the sensor is maximized and your running costs are optimized. For the little maintenance that remains please refer to chapter 7.

Aqueous samples

A simple pH electrode is sufficient for routine measurements in chemistry labs where a lot of aqueous chemical solutions are tested. The advantage of the simple pH electrode is that it is very easy to use and is also very robust. In general, these electrodes are made of glass and have a ceramic junction. They are also refillable, which means that you can refill the electrolyte thereby cleaning the electrode and prolonging its lifetime. An electrode of choice for these simple lab measurements is the **InLab® Routine** with or without temperature sensor. The **InLab® Routine Pro** has an integrated temperature sensor for automatic temperature measurement and compensation during measurement.

Samples of unknown composition, containing suspended matter and colloids

Figure 3: InLab® Expert electrode.

Measuring the pH of such samples can be somewhat tricky, since the dirt in the sample can hinder correct measurements. Examples of such applications are soil acidity measurements, quality control in foodstuffs such as soups and measurements in colloidal chemical systems. The risk of blockages with such samples would be very high if one were to use a pH electrode with a ceramic junction. Therefore it is best to use a pH electrode with an open junction such as the **InLab® Expert** which has a solid state polymer reference electrolyte. This electrode has an open junction which allows direct contact between the electrolyte and sample. For temperature compensation during the measurement it is possible to use an electrode with a built-in temperature sensor such as the **InLab® Expert Pro.**

Emulsions


Figure 4: InLab® Science electrode.

Another class of samples that require special care when doing pH measurements are emulsions, for example paints, oil in water dispersions, milk and other dairy products. Such samples can also block the junction of pH electrodes when the dispersed phase of the emulsion (the 'mixed-in' part) blocks the junction. The emulsion particles which can cause blockages are very small; therefore it is not necessary to measure with an open junction. Since electrodes with solid state polymers have relatively slow reaction times compared to electrodes with a liquid electrolyte, it is best to measure emulsions with electrodes that have a sleeve junction. The sleeve junction cannot be blocked easily and has a large contact area with the sample. If the junction should get blocked, it can easily be cleaned by moving the sleeve away from the junction and cleaning the electrode.

An example of this kind of electrode is the **InLab® Science**, or the **InLab® Science Pro** which has a built-in temperature sensor. Electrodes with a sleeve junction have a large contact area between the reference electrolyte and sample solution and therefore are also suitable for samples which cause an unstable signal.

Semi-solid or solid samples

Figure 5: InLab® Solids electrode.

Standard pH electrodes are generally not able to withstand the pressure of being pushed into a solid sample; therefore one needs a special electrode which is able to penetrate the sample in order to measure the pH. The shape of the membrane is also important as it needs to be formed in such a way as to ensure a large contact area with the sample, even if the electrode is pushed into the sample with force. The METTLER TOLEDO electrodes most suitable for these kinds of applications are the **InLab® Solids** or **InLab® Solids Pro**. While their spear shaped point enables them to pierce the sample, the membrane shape ensures accurate measurements. The **InLab® Solids** also has an open junction, which further prevents the junction from being blocked by the (semi-) solid sample. This electrode is typically used for quality control or checking production processes of cheese and meat.

Surfaces

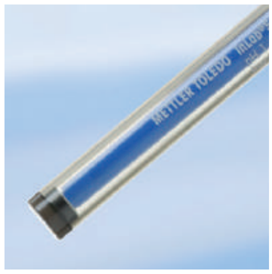

Figure 6: InLab® Surface electrode.

One sometimes needs to measure the pH of a sample with a volume so small that it doesn't cover the tip of a pH electrode. For these kinds of measurements there is only one solution, namely a flat pH electrode. This electrode only needs a surface to be able to measure pH. Applications for this type of electrode include the determination of the pH of skin during a health check-up and the pH of paper as required in the manufacture of archival grade paper for important documents. There are many other applications where only very small volumes are available for pH determinations, such as when measuring the pH of a drop of blood. Here the flat pH electrode is placed directly on the drop spreading out the sample over the surface of the flat membrane. Other applications involve very expensive biochemical samples of which only a tiny amount is available. The METTLER TOLEDO electrode best suited for this purpose is the **InLab® Surface.**

3 Ideally Equip Your pH Meter for Reliable Results

3.1 Stirring is key

A relatively inexpensive but very effective way of achieving faster and more reproducible results is to use a stirrer. There are 3 main reasons for that:
1. the human influence is reduced, e.g. placement of the sensor
2. the samples are homogenized, or at least better than without stirring
3. the temperature distribution is better, equilibrium is reached sooner

Ideally the same stirring conditions are used for both the calibration as well as the actual measurement. The reason for this is that the flow rate at the tip of the sensor has an influence on the pH potential, mainly on the reference's side.

Both the SevenCompact and SevenExcellence product lines offer powerful stirring options. The shared functions and differences are shown in the following table:

Function	SevenCompact	SevenExcellence
Stirring during calibration	Yes	Yes
Stirring before measurement	Yes	Yes
Stirring during measurement	Yes	Yes
General stirring speed (set for cal and meas)	Yes	
Method (sample) depended speed		Yes
Stirring only (without subsequent measurement)		Yes
Multiple stirring during one method		Yes
Use of overhead stirrer for viscous samples	Yes	Yes

Table 2: Stirring options on SevenCompact and SevenExcellence

The big advantage of the STIR method function in SevenExcellence is that you can stir more rigorously before a measurement to homogenize your sample, and then use the same stir speed as used for the calibration during the actual measurement to achieve accurate and precise results in a short time.

3.2 The use of a sample changer

The best way to get reproducible results is the use of a sample changer. Full automation excludes human influence on the individual results. If options like consistent stirring, automatic rinsing and auto end point are used, anyone can achieve the highest possible precision. The initial investment is amortized shortly, particularly when running measurements over night or weekends.

4 Best Deal with the Influence of Temperature

pH results are only correct if the sample temperature is taken into account. With these simple but effective rules for avoiding negative temperature effects, it's easy to obtain accurate, reproducible results.

Figure 7: Temperature sensor of an InLab® electrode.

4.1 Automatic temperature compensation (ATC)

ATC works best with normal-size samples.

- Use a sensor with integrated temperature probe and wait for a stable signal. The meter automatically corrects the pH signal. ATC works best in samples larger than 10 mL.

- Any "Pro" type InLab® sensor – InLab® Micro Pro, Science Pro, Expert Pro – has integrated temperature probes, eliminating worries over wrong temperature settings or not capturing temperature.

- For sensors without an integrated temperature probe, using a separate temperature probe is recommended.

4.2 Manual temperature compensation (MTC)

Figure 8: Temperature and MTC indication on a pH meter.

MTC is extremely accurate, but can be time-consuming.

- If the temperature of your sample is known (you are working in a climate-controlled room or the samples just came out of the refrigerator) enter this known temperature in the measuring settings of your instrument to correct the pH signal.

- When measuring samples with different temperatures, MTC can be time consuming, because the setting must be changed with every temperature change.

4.3 Measure the sample, not your sensor

With very small samples, the sample mass is negligible compared with the sensor mass. Thus, the sensor temperature can be wrongly interpreted as the sample temperature and the sensor can take long to reach equilibrium. Make sure temperatures of sample and sensor match. Best practice is to keep the sensor with the sample by storing them in the refrigerator or incubator, or at room temperature. This guarantees the highest accuracy because the pH membrane, reference system and sample are at the same temperature.

5 How to Deal with Some Really Tricky Cases

5.1 Measuring small samples

The more precious or rare the sample, the greater the challenge to use it for analysis. Some pH applications call for an electrode which only needs a small sample volume or can reach into difficult sample vessels, such as when measuring pH values in test tubes, Eppendorf tubes or narrow NMR sample tubes. Such containers with small sample volumes generally require a small and narrow pH electrode which can reach the sample and allow for pH determinations.

METTLER TOLEDO's micro and semi-micro pH sensors fit any size of sample container – particularly handy for precious or rare samples because they eliminate the need for larger volumes in electrochemical analysis.

InLab® Nano – cutting edge pH technology

The InLab® Nano measures pH in volumes as small as 5 µL. Its steel needle does not break easily, despite its super small diameter of 1.7 mm. Its slanted tip protects the pH membrane against mechanical damage, at the same time allowing for puncturing septa.

Figure 9: Detail of InLab® Nano electrode.

InLab® Ultra-Micro – an evolved micro sensor

Compared to the InLab® Micro, this electrode has a shorter sensor shaft of 40 mm for easier handling and less breakage. The ceramic junction is placed lower in order to make it possible to measure small sample volumes down to 15 µL, e.g. in well plates, centrifuge vials etc.

Figure 10: Detail of InLab® Ultra-Micro electrode.

InLab® Micro – the tried and trusted classic

The InLab® Micro is ideal for measuring pH in deep vials and centrifuge tubes thanks to its 60 mm long shaft. Rigorously tried and tested, it reliably meets most standard micro applications. It has become a true classic amongst the InLab® Micro family.

Figure 11: Detail of InLab® Micro electrode.

InLab® Micro Pro – temperature corrected pH

The InLab® Micro Pro has an integrated temperature sensor supporting automatic temperature compensation (ATC). The position of the temperature probe close to the pH membrane enables exact ATC.

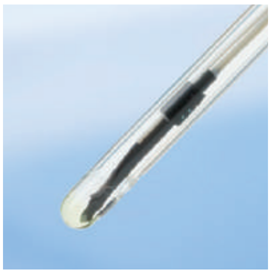

Figure 12: Detail of InLab® Micro Pro electrode.

InLab® Semi-Micro – maintenance and contamination free pH measurements

The InLab® Semi-Micro contains the latest in polymer electrolytes: XEROLYT® EXTRA. Service and operation could not be simpler thanks to the polymer electrolyte and the open reference connection. With no junction, there is no possibility of contamination or blockage.

Figure 13: Detail of InLab® Semi-Micro electrode.

InLab® Flex-Micro – pliable pH precision

This pH electrode will flex before breaking, so no more headaches over damaged micro electrodes. Relax knowing that one wrong move will not result in an expensive electrode replacement. An efficient member of the team.

Figure 14: Detail of InLab® Flex-Micro electrode.

InLab® Redox Micro – easy oxidation-reduction potential

ORP (oxidation reduction potential), also known as redox potential, is important in biology and easily determined with the InLab® Redox Micro. This traditional INGOLD product is based on the tried and true platinum ring design.

Figure 15: Detail of InLab® Redox Micro electrode.

	Minimum sample volume in this specific container type		
Electrode diameter	**1.7 mm**	**3.0 mm**	**3.0 mm**
Electrode type	**InLab® Nano**	**InLab® Ultra-Micro**	**InLab® Micro**
Container type and typical sample volume			
Small test tubes > 2 mL	50 µL	100 µL	200 µL
LiteTouch tubes 1.5 – 1.7 mL	20 µL	25 µL	65 µL
Sample tubes 0.5 mL	20 µL	25 µL	65 µL
96 well plates 200 – 300 µL	10 µL	20 µL	45 µL
384 micro plates 50 – 100 µL	5 µL	15 µL	–

Table 4: Minimum sample size for pH measurement

5.2 Non-aqueous, low ionic strength or very viscous samples

For certain challenging applications it is advantageous to use an electrode with SteadyForce® reference. The **InLab® Power** and **InLab® Power (Pro)** has been designed so that the inner electrolyte is under pressure, which has the advantage of preventing the sample from getting into the electrode regardless of the characteristics of the sample or application. This means that the measurements are both reliable and fast since the electrolyte flow is always sufficient for stable measurements.
For very viscous samples the **InLab® Viscous** works best: the combination of SteadyForce reference and specially designed tip allows for quick measurements despite the applicative challenges.

5.3 Biohazard: Clean with RNase and DNase cleansers and autoclave

The pH electrode models InLab® Power, Power Pro, Viscous and Viscous Pro can be sterilized by autoclaving. By cleaning the sensors with RNase and DNase decontamination solutions first, the potential for biological contamination is significantly reduced.

Figure 16: Special InLab® sensors can be autoclaved.

5.4 Contamination control of pH electrodes

When measuring samples there is always the risk of contamination, either by sample carry-over or by microbiological or genetic contamination. Conventional pH electrodes can also be damaged by electrolyte out-flow when measuring TRIS-based buffers or proteinaceous samples. This is not the case when working with InLab® electrodes.

Avoid sensor contamination with TRIS buffers

Accurate pH measurement is a key factor in buffer quality. TRIS-based buffers – widely used in biological research ranging from molecular biology to histology – can damage standard pH equipment.

How does TRIS do its damage?

When measuring pH during TRIS buffer preparation, the reference junction on conventional pH electrodes can clog when TRIS reacts with silver ions in the fill solution. This reaction can also occur with protein in the buffer, such as BSA (bovine serum albumin). The eventual consequences are slow or fluctuating readings, or even entirely wrong results.

InLab® electrodes by METTLER TOLEDO are specifically designed for compatibility with TRIS-based buffers, assuring reliable results and accurate buffer values. The electrolyte in InLab® electrodes is guaranteed to be free of silver ions, eliminating the possibility of contamination.

Figure 17: SevenExcellence meter and InLab® electrode during calibration.

6 Perform an Easy System Check and Troubleshoot

pH troubleshooting

Locating the problem of a pH measuring system that has suddenly started performing badly is the first step to restoring it to its original level of performance.

Where could the problem lie?

With the meter set to read mV, dip the electrode into pH 7 buffer. The reading should be 0 mV ±30 mV with an Ag/AgCl reference. Next read a pH 4 or pH 10 buffer – the solution should be greater than 150 mV different from the pH 7 potential. If not then test the following…

Application

Are you using the right electrode for your application? There are different types of pH electrodes for special applications: non-aqueous, low conductivity, TRIS etc. To make sure that you are using the right electrode visit the METTLER TOLEDO Sensor ProductGuide at: **www.electrodes.net**

Operator

It is sometimes worthwhile to check the obvious:

- Is the unit properly grounded or plugged into the wall outlet?
- Are the electrodes plugged into proper terminals and seated firmly?
- Is the meter properly calibrated with the correct buffers?

Before taking a measurement, check that the wetting cap has been removed and that the side filling aperture is open. Remember to rinse the electrodes before measuring a different buffer or sample.

pH Meter

Test the pH meter with the shorting clip (standard delivery) or Test Plug Set. If this plug does not set the potential to 0 mV, the meter may be the problem. In this case call METTLER TOLEDO Service.

Buffers

Ensure that you are using the correct buffers in the correct sequence. Always use fresh buffers. Check expiry date.

Cable and Connector

Test your detachable cable by replacing it with an identical one. If you do not have a spare cable or are using a hard wired electrode, then check to see whether there is a change in the signal on the instrument when you bend the cable.

Inspect and clean all connectors including the meter socket. If you are using an electrode with a MultiPin™ or S7 connector, make sure that they are free from KCl crystals or other deposits. Dirty or corroded connectors lead to erroneous readings.

Electrodes

Visual inspection of the electrode can often provide important clues about the cause of the problem:

Filling solution

- Ensure that the electrolyte level is above the internal elements.
- Empty, rinse and refill the electrode reference chamber.
- Ensure that you are using the correct electrolyte as written on the electrode shaft or in the operating instructions, and that the electrolyte fill port is open.

Air bubbles

- Check for air bubbles inside the electrode. If some are present remove them by gently shaking the electrode downward or in the case of electrodes with gel electrolyte placing the electrode upright in warm water.

Blocked junction

- Are there visual signs of blockage or discoloration of the reference junction?
- Hang the electrode in the air for 30 minutes to check whether the electrolyte flows through the junction. If no KCl creeping is visible, it is a sign that the junction is clogged and must be cleaned. Then do the following:

a) Soak the electrode in hot (50 °C – 60 °C) electrolyte for a few minutes. If this does not work then …
b) … soak the electrode overnight in 0.1 mol/L HCl.
c) For protein contamination, soak the electrode in Pepsin–HCl solution.
d) For sulfide contamination, soak the electrode in Thiourea solution.
e) As a last resort, soak the electrode in ammonium biflouride regeneration solution for approx. one minute.

See chapter 7.2 for more details.

7 Maintain Your Equipement for Maximum Uptime

7.1 Care and Measurement Technique

This section provides an overview of how to properly care for pH sensors and some hints regarding measurement techniques. In everyday use it is crucial to have the pH electrode in good shape. This is the most effective way of working efficiently and to save time.

pH electrode maintenance

Regular maintenance is very important for prolonging the lifetime of any pH electrode. Electrodes with liquid electrolyte need the electrolyte to be topped-up when the level threatens to become lower than the level of the sample solution. This way a reflux of the sample into the electrode is avoided. The complete reference electrolyte should also be changed regularly, e.g. once a month. This ensures that the electrolyte is fresh and that no crystallization occurs despite evaporation from the open filling port during measurement.
Be careful not to get any bubbles on the inside of the electrode, especially near the junction. If this happens the measurements will be unstable.
To get rid of any bubbles, gently shake the electrode in the vertical motion like with a fever thermometer.

Electrode storage

ReElectrodes should always be stored in aqueous and ion-rich solutions. This ensures that the pH-sensitive gel layer which forms on the pH glass membrane remains hydrated and ion rich. This is necessary for the pH membrane to react in a reliable way with respect to the pH value of a sample.

Short term storage

In between measurements or when the electrode is not being used for brief periods of time, it is best to keep the electrode in a holder containing the special InLab® storage solution[1], its inner electrolyte solution (e.g. 3 mol/L KCl), or in a pH 4 or pH 7 buffer. Ensure that the level of solution in the beaker is below that of the filling solution in the electrode.

Long term storage

For long term storage, keep the electrode wetting cap filled with the InLab® storage solution[1] or, alternatively, with the inner electrolyte solution, pH buffer 4 or 0.1 mol/L HCl. Make sure that the filling port for reference and combination electrodes is closed so as to avoid loss of the electrolyte solution through evaporation, which can cause the formation of crystals within the electrode and junction.
Never store the electrode dry or in distilled water as this will affect the pH-sensitive glass membrane and thus shorten the lifetime of the electrode.
Although an electrode that has been incorrectly stored can be restored by regeneration procedures, following the above mentioned recommendations will ensure that your electrode is always ready to use.

Temperature sensors

Rinse the temperature sensors after use and store dry in the packing box to prevent damage.

---

[1] This InLab® storage solution can be ordered from METTLER TOLEDO (30111142)

7.2 pH electrode cleaning

To clean the electrode, rinse it with deionized water after each measurement but never wipe it clean with a tissue. The rough surface of the paper tissue will scratch and damage the pH-sensitive glass membrane removing the gel-layer and creating an electrostatic charge on the electrode. This electrostatic charge causes the measured signal to become very unstable. Special cleaning procedures may be necessary after contamination with certain samples. These are described in greater detail below.

Blockage with silver sulfide (Ag_2S)

If the reference electrolyte contains silver ions and the sample being measured contains sulfides, the junction will get contaminated with a silver sulfide precipitate. To clear the junction of this contamination, clean it with 8% thiourea in 0.1 mol/L HCl solution.[1]

Blockage with silver chloride (AgCl)

The silver ions from the reference electrolyte can also react with samples that contain chloride ions, resulting in an AgCl precipitate. This precipitate can be removed by soaking the electrode in a concentrated ammonia solution.

Blockage with proteins

Junctions contaminated with proteins can often be cleaned by immersing the electrode into a pepsin/HCl (5% pepsin in 0.1 mol/L HCl) solution for several hours.[2]

Other junction blockages

If the junction is blocked with other contaminations, try cleaning the electrode in an ultrasonic bath with water or a 0.1 mol/L HCl solution.

pH electrode regeneration and lifetime

Even electrodes that have been well maintained and properly stored may start performing poorly after some time. In such cases it may be possible to regenerate the pH-sensitive glass membrane and restore the electrode to its previous level of performance using an ammonium bifluoride regeneration solution[3]. This regeneration solution is based on a highly diluted solution of hydrofluoric acid which etches away a very thin layer of the glass membrane, exposing a fresh surface area.

When using the regeneration mixture, do not to leave the electrode in the solution for longer than 1 – 2 minutes or the whole pH-sensitive membrane will be corroded away and the electrode rendered useless.

The expected lifetime of a correctly used and maintained pH electrode is around one to three years. Factors that contribute to a reduction of the lifetime of an electrode include high temperatures and measuring at extreme pH values.

[1] This thiourea solution can be ordered from METTLER TOLEDO (51340070)
[2] This pepsin solution can be ordered from METTLER TOLEDO (51340068)
[3] This regeneration solution can be ordered from METTLER TOLEDO (51350104)

Good Measuring Practices
Five Steps to Improved Measuring Results

The five steps of all Good Measuring Practices guidelines start with an evaluation of the measuring needs of your processes and their associated risks.
Using this information, Good Measuring Practices provide straight forward recommendations for selecting, installing, calibrating and operating laboratory equipment and devices.

- Preservation of the accuracy and precision of results
- Compliance with regulations, secure audits
- Increased productivity, reduced costs
- Professional qualification and training

Good Electrochemistry Practice™
Reliable pH measurements – thanks to GEP™

Learn more about Good Electrochemistry Practices program

www.mt.com/GEP

www.mt.com/SevenExcellence

For more information

Mettler-Toledo AG, Analytical
CH-8603 Schwerzenbach, Switzerland
Tel. +41 22 567 53 22
Fax +41 22 567 53 23

Subject to technical changes
© 11/2014 Mettler-Toledo AG
Global MarCom Switzerland