Benefits of fully automating the titration process

In volumetric analysis, the operator has to perform various steps. Most automatic titration automation solutions cover only some of these steps, such as the titration itself and the changing of samples. In order to achieve a significant gain in productivity, it is also important to automate procedures like sample preparation. Automating the whole chain of steps makes unattended automatic analysis possible.

The analysis process
The analysis process in titration involves various steps of differing complexity. At the beginning of an analysis, the accurate weighing of a solid or the precise measurement of the volume of a liquid sample is crucial for the accurate determination of the sample content. The sample then has to be properly prepared, i.e. transformed physically or chemically into a state suitable for analysis. It is then transferred to the titrator where the volumetric determination of the sample content takes place. The sample reacts with appropriate reagents and undergoes a fast, single, complete and stoichiometric chemical reaction under the given conditions. Finally, the result, i.e. the content is calculated, documented, and stored.
**Automation of titration analysis: better reproducibility**

Almost all the steps of the analysis process can be automated, i.e. the steps can be defined as a sequence of individual operations (titration method) that are performed independently without manual intervention. Usually, the sample preparation performed by a titrator consists of dissolving the sample or allowing a chemical reaction to take place by stirring at a predefined speed for a fixed period of time. Afterward, the pH and temperature of the sample solution can be measured and documented, or used to perform a predefined adjustment to the values necessary for the titration, e.g. a pH value adjustment. The titrator controls the entire titration, including the termination of the analysis and the evaluation of the results. In addition, calculation(s) and the documentation, transfer and storage of data are done automatically. An automated titrator also provides for the activation of external devices or auxiliary instruments like pumps, an immersion heater, sampling units and, of course, a sample changer.

The benefits of automated titration over manual titration are obvious:

- The analysis procedure becomes much less operator dependent, thereby increasing the reproducibility.
- Each sample is titrated in exactly the same way because the control parameters of the titration defined in the method do not change. This enhances the repeatability.
- The minimum increment size is much smaller than in a manual titration. This leads to a higher resolution of the titration curve, thereby improving interpolation between increments. This increases the accuracy of the results.
- Errors in calculations and documentation are minimized.

**Automating an automatic titration: the titrator/sample changer combination**

Do the benefits gained by using a titrator really save time and allow the user to do other tasks or analyze more samples? Do these benefits help him become more productive? A closer comparison shows that a titration performed using a titrator does not necessarily take less time than an experienced analyst performing the same titration manually. Furthermore, the time required for the titration is usually not long enough for him to perform other tasks at the same time. In addition, chemists like to observe the progress of a chemical reaction, i.e. they tend to watch the titrator during the titration process. In summary, a titrator definitely increases the precision, accuracy and handling of an individual analysis, but the gain in productivity is still rather small.

The first step toward the complete automation of titration is achieved by connecting the titrator to a sample changer. The titrator controls the sample changer via the titration method. This defines all the information necessary to perform the desired operations, e.g. go to next sample, rinse the sensor, pump an auxiliary reagent or an additional solvent to dilute the sample. The sample changer performs, step by step, all the operations necessary for the analysis of the samples on the tray.
Applications

The new Rondo 60 sample changer:
Three selected applications

The new Rondo 60 sample changer is based on a very modular concept - the basic unit can be expanded with a second titration tower, pumps and external devices such as high speed homogenizers in order to meet the various requirements for developing a titration method. A second titration tower can also be used to perform sample preparation prior to titration, or for the measurement of multiple parameters that necessitate a separation of the sensors (e.g. conductivity and pH value in water analysis). Three applications are presented below to illustrate the Rondo 60’s flexibility:

Determination of acid and base Number
AN (Acid Number) and BN (Base Number) determinations are important analyses in refineries, petrochemical industries, and in power stations. The AN is also known as the neutralization number. It is a measure of the quantity of KOH necessary to neutralize the acidic constituents in the oil. It is used to assess the state of gear, hydraulic or rotary oils. On the other hand, the BN is an indication of the concentration of constituents with alkaline effects (e.g. additives) that can neutralize acid forming impurities.

The exact determination of AN/BN is crucial for manufacturers and users of mineral oils and derived products because the presence of acidic constituents can corrode and damage the production facilities. This can be monitored in advance by the AN determination.

The analytical procedure is not only limited to the titration of the sample. It also consists of sampling and appropriate sample preparation before titration. After sampling, i.e. collecting a representative bulk sample from the material to be analyzed, a smaller homogeneous laboratory sample is prepared, e.g. by grinding and dissolving a powder in an appropriate solvent (sample preparation). From this, small test portions (aliquots) are transferred to the titration beakers that are then placed on the sample changer tray for individual analysis.

If sample preparation and sample transport are also automated, a number of decisive benefits are gained. A sample changer should be able to do more than just “change samples”. Other important tasks are for example preparing samples, switching external devices, delivering or removing solvents, cleaning and conditioning sensors. In other words, automating a titrator with a sample changer enables a large batch of samples to be analyzed in unattended operation, and the analyst is free to do other jobs. The new METTLER TOLEDO Rondo 60 sample changer allows the titration analysis to be completely automated.

The costs of such a system are certainly higher than an automated solution with a titrator. However, even a rather conservative calculation for a titrator/sample changer combination that assumes a time-saving per sample of 10-15% at a sample throughput of 20 samples per day proves that the investment pays for itself in less than a year.

In summary, a titrator/sample changer combination leads to a large increase in productivity because the periods of unattended operation are longer. The analyst can even perform analyses overnight. The payback period is less than a year, even at a moderate sample throughput of 20 samples per day.

Fig. 1: The SAN/AN determination principle.
The importance of these analysis techniques is evident in the multitude of national and international standards and regulations, e.g. ASTM.

Figure 2 illustrates the principle and basic steps of an AN analysis:

1. **Acid Number (ASTM D 664/95)**
   - In this analysis, appropriate cleaning of the sensors is crucial for achieving accurate and reproducible results. Thanks to the magnetic coding of the Rondo 60, one or more conditioning beakers can be defined to rinse and condition the electrode thoroughly before the next sample. Rinsing is performed by additional pumps in combination with a new rinsing system, called Power Shower™ that allows the sensor to be cleaned from top to bottom.

2) **pH, alkalinity (Tower A)**
   - A DG114 electrode (electrolyte: 2 M KNO3) is used as the indication electrode, and the sample is titrated with 0.1 M HNO3 to fixed endpoints EP = pH 8.2 or pH 4.3. The electrode is connected to sensor input 3 of the DL7x titrator.

3) **Chloride determination (Tower A)**
   - The chloride content is determined by titration with 0.1 M AgNO3, and indication using a DM141 electrode (connected to sensor input 2).

4) **Calcium and magnesium determination (Tower A)**
   - Calcium and magnesium are determined separately by complexometric titration with 0.01 M EDTA (0.1 M) and a DX240 calcium ion-selective electrode DX240 (connected to sensor input 1). Before starting the titration, a buffer solution of acetylacetone/TRIS (pH 8.5) is added to the sample to enable the two equivalence points to be distinguished (see Application Brochure No. 1, ME-724492). The reference half-cell of the DG114 is also used as a reference for the DX240 using the cable ME-51'089'954. This cable allows the reference half-cell of the DG114 to be connected to the reference input at sensor input 1 of the DL7x titrator by a conventional 4 mm banana-banana cable.

These steps can be completely automated with a Rondo 60 and a DL7x titrator. The methods used to determine the buffer values, the blank, and the SAN/AN numbers are defined in the titrator and run as a list of methods. If then conditions of the DL7x allow the Titrator to decide whether an analysis has to be stopped in case the electrode is not in a suitable condition.
Automated water determination by Karl Fischer titration

While a second titration tower increases the application possibilities of the sample changer, the flexibility can be still further improved using different titration beakers. For instance, the Karl Fischer titration for the determination of water can also be automated by means of special beakers and a special titration set (see Fig. 2).

The Karl Fischer set is based on a very simple but effective idea - the beaker is sealed with foil and a rubber sealing ring. This almost completely eliminates the penetration of ambient moisture into the titration beaker, which would have an adverse effect on the results. The foil is pierced by the electrode at the start of the titration.

Conclusions

Automation has become a very important part of modern titration. Not only can a quantitative analysis be automated by microprocessor-controlled titrators, but sampling and sample preparation can also reach a high degree of automation with the use of modern sample changers of modular design. This results in much enhanced flexibility, and means that sample changers can satisfy the requirements for automation for a very wide range of different applications.

Together with the METTLER TOLEDO DL5x and DL7x series titrators, the Rondo 60 is a very flexible, easy-to-use system that is ideal for most automation tasks. The modular concept of the Rondo 60 allows the complete automation of the titration procedure, thereby enabling a high sample throughput to be achieved.

This frees lab personnel from routine work. The measurements can be performed more rapidly and more reliably because operator errors are largely eliminated, and contact with hazardous chemicals is reduced to a minimum. Unattended operation is also possible, allowing samples to be analyzed around the clock by shift operators. The longer periods of unattended operation means that the operator can now perform other more demanding tasks, which in turn increases the productivity of the analytical laboratory.
Water is essential to all life on earth. Human beings in particular need water that is readily available, not only for consumption but also for agriculture and industry. The availability of potable water is, however, limited. As the world's population increases, more and more water is polluted every year, but at the same time the need for clean drinking water increases. The result is that the regeneration cycle of water is shortened. Water monitoring has therefore become essential. Since water control plays such an important role, it is absolutely essential to have equipment that meets all the specific measuring requirements.

Rivers represent an important part of the regeneration cycle. Because they flow above ground and usually pass over natural or artificial steps and rocks, they contain a lot of dissolved oxygen. The processes of nitrification and decomposition of carbonaceous compounds are therefore enhanced. The concentration of dissolved oxygen and the temperature of a river are good indications of the river's regeneration capacity. Other parameters such as pH, conductivity and oxidation/reduction potential (ORP) are more direct indications of the actual state of a river. This also applies to ion-selective measurements such as nitrate measurements. With the new METTLER TOLEDO X-matePro, all these parameters can be measured on-site within a very short time frame. Its modular design enables a complete and fast spot check to be made even in systems with rapid fluctuations.

The River Toess

Such a multiparameter spot check was done along a section of the river Toess in July of this year. The Toess is a small river in Switzerland that flows into the River Rhine. It begins at about 1000 m above sea level and flows through open fields in a fairly wide valley. Further downstream, the river is largely covered by trees until an altitude of approximately 490 m is reached where it flows through a forest. It then enters a densely populated region before finally joining the Rhine at an altitude of about 400 m above sea level.

The parameters shown in Table 1 were measured with the X-matePro. For the purpose of our study, readings were taken at three points along the River Toess, beginning at 700 m and ending at 490 m. All measurements had to be taken within a time frame of one hour for the results to be meaningful.

The Toess was measured at three points. Automatic temperature compensation (ATC) was used for the pH measurements. The pH values listed below therefore reflect the actual pH value of the water. The conductivity values were also measured using ATC. The values were referenced to a temperature of 25 °C. The ion-selective measurements were performed using the same temperature as for the pH readings. These temperature values were entered manually (MTC).
The pH value does not change significantly over the stretch of the river analyzed. This is a rough indication that the composition of the water does not undergo major changes, e.g. due to the inflow of industrial wastewater. The conductivity value represents the total ion content of the water. Since salt cannot be eliminated in purification plants, it accumulates along the course of the river. Wherever the river flows over artificial steps and natural rocks, the percentage of dissolved oxygen immediately increases, enabling the river to regenerate faster.

Where the river flows through the forest (measuring point 3), the air temperature decreases while the relative humidity increases. The ammonium values are very low in the upper part of the river since there is hardly any human influence. In the lower part of the river between measuring points 2 and 3, there is an influx of water from a purification plant.

This water contains very little ammonium because the elimination process of the purification plant is very efficient. Technically, nitrate is not so easy to eliminate as ammonium in a water purification process. The concentration of nitrate at point 3 is therefore higher.

All readings were performed using an X-mate® with interchangeable modules. Conductivity was measured using an InLab®781, pH with an InLab®482, dissolved oxygen with an InLab®681, ORP with an InLab®581 and humidity with an InLab®986. A BNC module was used for the ion-selective measurements. These components all fit in a handy portable field case (see Fig. 3), making it easy for a person to measure all the values in a short period of time. The analyses showed that the River Toess is a very clean river even though it flows through populated areas.

Table 1. Parameter readings along the River Toess

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Point 1</th>
<th>Point 2</th>
<th>Point 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (ATC)</td>
<td></td>
<td>7.94</td>
<td>8.23</td>
<td>8.03</td>
</tr>
<tr>
<td>Conductivity (ref. 25 °C)</td>
<td>µS/cm</td>
<td>428</td>
<td>443</td>
<td>524</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>%</td>
<td>58.7</td>
<td>81.2</td>
<td>79.2</td>
</tr>
<tr>
<td>Ammonium (MTC)</td>
<td>ppm</td>
<td>0.6</td>
<td>8.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Nitrate (MTC)</td>
<td>ppm</td>
<td>8.7</td>
<td>7.4</td>
<td>11.4</td>
</tr>
<tr>
<td>ORP</td>
<td>mV</td>
<td>251.5</td>
<td>283.1</td>
<td>286.7</td>
</tr>
<tr>
<td>Water temperature</td>
<td>°C</td>
<td>18.8</td>
<td>18.3</td>
<td>17.2</td>
</tr>
<tr>
<td>Air temperature</td>
<td>°C</td>
<td>26.8</td>
<td>26.7</td>
<td>24.5</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>%</td>
<td>47.9</td>
<td>55.9</td>
<td>64.1</td>
</tr>
</tbody>
</table>

Fig. 3: The author taking measurements. Note the X-mate field case in the foreground.

Fig. 4: The modular design of the X-mate® is very convincing.
Optimum parameters for the titration III: Termination of the titration and the choice of the correct evaluation procedure

So far in our series on titration parameters, we have reached the stage of titrating with the correct control parameters resulting in the best shape curve, and ensuring the correct recognition of the equivalence point. What remains is the termination criteria of the titration and evaluation of the equivalence point.

Termination of the titration
A powerful feature of the METTLER TOLEDO general-purpose titrators is their ability to use various termination criteria:
- to stop as soon as the required number of equivalence points have been detected,
- to stop when a fixed potential or pH has been reached,
- to stop only when the slope of the curve has dropped below a given value,
- to stop when the total titrant consumption reaches a certain factor times the sample size (or % of the nominal consumption).

In addition, there is one further “emergency stop” criterion, namely when maximum volume is reached. This is to prevent both overfilling the titration beaker and wasting titrant.

These termination criteria can be used in combination or as single criteria. If multiple criteria are chosen, the titration will be terminated as soon as the first condition is reached. By activating the “Combined Termination Criteria” parameter, the titration will only be terminated once all of the selected conditions (excluding “Maximum Volume”) are met. This is particularly useful when one would like to stop immediately after the first equivalence point but would still like to see the overall curve shape.

For example, assume that you have chosen to stop after one equivalence point (Fig. 1). By combining this with termination at slope a better overview of the titration curve (Fig. 2) is obtained. With the above combination it is also possible to titrate using “Steepest jump only” (see UserCom 4) without having to titrate to a maximum volume. To do this, “Steepest jump only” and combined termination criteria of “Stop after n EQPs” together with “Terminate at slope” are chosen.

Evaluation of the titration curve
The choice of the correct evaluation procedure depends primarily on the shape of the titration curve. For the classical S-shaped curve, many procedures have been described to determine the equivalence point. These include approximation, interpolation and mathematical procedures such as nonlinear regression and curve fitting. The approximation and interpolation pro-

Fig. 1: Termination after 1st equivalence point
Fig. 2: Combined termination criteria
nonlinear regression procedure is used that yields the “true” equivalence point. This procedure is ideal for acid/base, argentometric, complexometric and some REDOX titrations.

When curves are extremely asymmetric, the above procedures no longer yield the best evaluation of the equivalence point. This is true for some REDOX titrations with very sudden breaks, as well as for some photometrically indicated titrations. It has been found empirically, that in such cases, the true equivalence point lies between the inflection point and the section of the curve with the greatest curvature (smallest radius of curvature). Here, it is necessary to use an approximation procedure. One such method is the Tubbs procedure, where circles of radii to match the curvature of the two sections are drawn. The intersection of the line joining the centers of the circles with the titration curve is taken as the equivalence point (Fig. 3).

By choosing the “Asymmetric” evaluation procedure in the METTLER TOLEDO titrators, a mathematical variation of the Tubbs procedure (according to Ebel) is used. This procedure uses hyperbolae rather than circles and joins the foci rather than the centers of the circles. For this procedure to work, the titrator needs at least six measured points in the regions of greatest curvature both before and after the inflection point. If insufficient data points are present, the titrator will switch back to a standard evaluation automatically and will note this in the printout of the raw results.

The last two types of curves that the METTLER TOLEDO titrators are able to evaluate are both special cases due to the indication technique used. The first is the “Segmented” evaluation of typical conductimetric curves (Fig. 4) and the other is the “Min/max” evaluation of turbidimetric curves (Fig. 5).

Lastly, the METTLER TOLEDO titrators allow the determination of two interpolated endpoints in addition to any equivalence points. These are specified as “Buffer potential 1” and “Buffer potential 2”, with raw results QP1 and QP2.

All that is left to do in order to obtain the final result is to enter or select the calculation to use, and to specify exactly what should be sent to a printer or computer. This is covered in detail in the respective titrator operating instructions. Some tips on using advanced formula are given in this UserCom.
Rondo 60: a flexible system that can grow with the user’s needs

**METTLER TOLEDO** recently introduced the Rondo 60 sample changer. Combined with a METTLER TOLEDO Titrator of the DL5x or DL7x series, the Rondo 60 allows the titration of up to 60 samples without any user interaction. The most impressive feature of the Rondo 60 is its great flexibility. Starting from a standard configuration, the user can build the system that best fits his needs.

To learn more on the application possibilities of the Rondo 60 system, see pages 1 to 5 of this UserCom. The following article gives an overview of the various Rondo 60 accessories.

The Rondo 60 can be equipped with a second titration tower. If the second tower is placed opposite the first one (Fig. 1), the titration throughput can be doubled with a DL77 titrator. If the towers are placed side by side (Fig. 2), the user has more possibilities for sample preparation and can perform conductivity measurements and titrations at the same time. The towers can be placed on the left or the right side of the instrument depending on the user’s preference and the available workspace.

The Rondo 60 can be used with different sample racks, thereby allowing the measurement of different sample sizes. Apart from the rack for 20 standard METTLER TOLEDO beakers, racks can be added that allow the use of standard 150 ml, 250 ml and 400 ml glass beakers or any other beakers that fit (Fig. 3). Together with the optional SU24 sampling unit and the test tube rack, up to 60 samples can be analyzed automatically.

For sample preparation, a second membrane pump can be attached directly to the back of the tower. If a peristaltic pump is required, the METTLER TOLEDO SP250 can be connected. Each tower can be equipped with 1 or 2 pumps.
For moisture determination, the Karl Fischer Set is added to the standard Rondo 60 configuration (Fig. 6). In both cases, the instrument can be changed back to a standard instrument within minutes.

If aggressive chemicals are used, the Rondo 60 can be combined with the CoverUp™ Lid handling system. Because sample beakers are covered with a lid before and after titration, it is no longer necessary to perform titrations in a fume hood.

With the COD set, the Rondo 60 is easily converted into a specialist system for COD titrations (Fig. 7).

**Customer Courses: Hands-on training in Switzerland**

As one of our users you are in possession of a highly versatile instrument that allows you to perform the most complicated applications simply by pressing the RUN key. Do you constantly develop new methods, adapt parameters and calculations to suit your needs, know the pros and cons of all the titration methods and indication techniques - are you in command?

... or do you get the feeling that the instrument is sometimes doing what it wants?

- And have you ever wondered how you could get the titrator to perform other analyses?
- Do you want to know the ultimate truth about optimal parameter settings?
- In short: are you interested in learning more about the theory of titration and the use of our titrators?

Then why not visit one of our customer courses and spend 4 to 5 days of intensive titration training with our specialists.

For more information and registration please contact your local METTLER TOLEDO organisation.
Tips and Tricks

Powerful DL5x/DL7x calculation formulas - some examples

METTLER TOLEDO titrators have extremely versatile calculation functions. The flexible formulas allow much more than just simple calculations. Three more advanced examples that demonstrate the power of these calculation functions are presented below. Basic information on the use of formulas is given in the titrator operating instructions.

1. Using calculations to select the correct equivalence point

In mixtures of two or three different acids or in the case of polyprotic acids such as phosphoric acid, the selection of the correct equivalence is important for the calculation of the content of each of the constituents. For example, in order to determine the content of three different acids of increasing pKa values, a method is used that ensures the unambiguous assignment of the equivalence points to each of the acids, and that also takes into account the fact that a constituent might sometimes be missing. In this case, the titration is performed to a predefined maximum volume or pH, and the contents are calculated using the consumption identified by the condition:

\[
R1 = Q(3.0<\text{EPOT}<6.0) \cdot C/m \quad (or \ U \text{ for DL7x})
\]

In this way, the consumption to the equivalence point whose potential lies between pH 3 and 6 is used to calculate the content. For the second acid with a higher pKa, another range at higher pH values is used and so on.

2. Using the calculations to calculate statistics in periodic analysis

In a water laboratory, the m-value (methyl orange value, pH 4.3) of a water sample is determined. Three samples are titrated every hour (8 hours per day) with daily statistics. To do this, a method is run on a DL7x/Rondo combination with one sample using “List continuous”. Because of this, the programmed statistic function cannot be used and the method has to contain the formulas for the rolling mean and standard deviation in the calculation functions:

\[
s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}
\]

\[
x_i = \text{result of a sample}
\]
\[
\bar{x} = \text{mean value}
\]
\[
n = \text{number of samples}
\]

Since the mean value changes after each sample, it is not possible to use the standard equation without storing every result up to the point where the rolling mean and standard deviation have to be calculated. Rearrangement of the above equation yields the following:

\[
s = \sqrt{\frac{\sum_{i=1}^{n} x_i^2 - n \bar{x}^2}{n-1}}
\]

\[
x_i = \text{result of sample } i
\]
\[
\bar{x} = \text{mean value}
\]
\[
n = \text{number of samples}
\]

In the new equation, the mean value is separated from the sum so that the sum of the squares can be stored separately from the mean value, as an auxiliary value. This enables rolling statistics to be calculated.
A method for the determination of the m-value
The method shows the relevant functions for the calculation of rolling statistics. An auxiliary value function is introduced before the actual titration to serve as a sample counter. After each sample, the rolling mean value and the statistics are documented. After 8 hours or 24 samples, the counter and the sums are reset to zero, thus reinitializing the statistics. The process is controlled by three auxiliary value functions at the end of the method that are only executed when the condition “n = 24” is fulfilled.

3. The use of log and anti-log functions to calculate results in direct measurement with an ISE

The calibration of a pH or ISE electrode is a logarithmic function where the pX value (-log[X]) is plotted against the measured mV signal. When performing a direct measurement with an ISE, the mV signal is automatically converted into a pX value by the titrator. In order to convert the pX value to the desired unit, it is necessary to use an anti-log function. METTLER TOLEDO titrators include this anti-log function, denoted by “pw”, resulting in the calculation given below:

\[ R = \text{pw}(-E) \times C \]
\[ C = 1000 \text{ (if the standards concentration was given in g/L)} \]
\[ \text{Unit} = \text{ppm} \]

These three examples demonstrate the versatility of the calculation functions in METTLER TOLEDO titrators, enabling advanced calculations that involve square roots, logarithmic or exponential functions, etc. to be made. These special functions are available in titrators of both the DL5x and DL7x series. Together with the conditions included in most of the functions of the DL7x, the calculation functions provide an invaluable tool for the control and evaluation of a titration and thereby ensure that correct results are obtained every time.

pH electrode troubleshooting

The electrode is the key to successful analysis. Since the electrode is the only part of the analytical instrument that is in direct contact with the sample, its selection and maintenance (and therefore sensitivity) has the strongest influence on precise and accurate measurements. However, an electrode that has been correctly selected and that has been working properly may nevertheless suddenly start performing badly. In this article we will help you to identify possible reasons for this and suggest a number of procedures for restoring the electrode to its original performance.

Before beginning the diagnostic procedure
Before testing an electrode, make sure that the electrode cable and the instrument are working properly. Then examine the sensor closely. Visual inspection can very often provide important clues about the cause of the problem, e.g. a clogged diaphragm or an air bubble in the tip of the electrode.

Glass membrane
Diagnosis
One symptom may very often have various causes. The following table will help you to find out what caused your electrode to fail with regard to the pH-sensitive glass membrane:
### pH-Sensitive Glass Membrane: Symptoms, Causes and Procedures

<table>
<thead>
<tr>
<th>Symptom</th>
<th>Cause</th>
<th>Due to</th>
<th>Procedures for restoring the electrode</th>
<th>Explanations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced slope (&gt;80% - &lt;90%)</td>
<td>Ageing of glass</td>
<td>High temperature, age of sensor</td>
<td>Regeneration (see next page)</td>
<td>Highly probable</td>
</tr>
<tr>
<td></td>
<td>Scratches on membrane</td>
<td>Abrasion, solid particles, incorrect cleaning</td>
<td>Sensor cannot be repaired</td>
<td>Probable</td>
</tr>
<tr>
<td></td>
<td>Broken membrane or shaft</td>
<td>Mechanical or temperature shock</td>
<td>Sensor cannot be repaired</td>
<td>Possible</td>
</tr>
<tr>
<td></td>
<td>Gel layer destroyed or dehydrated</td>
<td>Ion deficient media, non-aqueous applications</td>
<td>Rehydration with electrolyte or tap water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dry storage of electrode</td>
<td>Wrong storage</td>
<td>Rehydration with electrolyte or tap water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcium on glass membrane (whitish film)</td>
<td>Measurement media</td>
<td>Dip sensor in conc. acetic acid until deposits are dissolved. Afterwards regeneration.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oil, fat or tar residues (visible?)</td>
<td>Measurement media</td>
<td>Clean sensor with degreasing agent, then rinse with water. If necessary, regeneration.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Deposits of unknown substances (visible?)</td>
<td>Measurement media</td>
<td>Clean sensor with suitable cleaning agent. If necessary, regeneration.</td>
<td></td>
</tr>
</tbody>
</table>

**Explanations:**
- **Highly probable**
- **Probable**
- **Possible**

*Table 1: pH-Sensitive Glass Membrane: Symptoms, Causes and Procedures*
**Regeneration procedure**

A reduced calibration slope as a result of changes in the gel-layer on the glass membrane can very often be observed with older electrodes or electrodes that have been stored dry. Similar effects are noticeable when an electrode is used for non-aqueous applications because the gel-layer is dehydrated. The pH-sensitive glass membrane is reactivated using a regeneration solution (METTLER TOLEDO order number 51340073). This solution is a mixture of hydrochloric (HCl) and hydrofluoric acids (HF).

Please note

Since these acids are extremely aggressive, make sure that you observe all the necessary safety precautions, e.g. wear protective goggles, a laboratory coat and chemical-resistant gloves. Keep the volume of solution to a minimum by using a small acid-resistant vessel.

Dip the tip of the electrode into the regeneration solution for 5 to 15 minutes. The maximum immersion point is level with the upper shoulder of the pH-sensitive glass (see Fig. 2). Never dip the sensor shaft into the solution because the hydrofluoric acid will damage it. Then rinse the electrode thoroughly with water and condition it for approximately an hour in a buffer solution of pH7. Finally, place the sensor overnight in the reference electrolyte specific to that sensor.

**Reference diaphragm Diagnosis**

Faulty electrodes often have a clogged diaphragm. In most cases, the diaphragm is visibly discolored. Some are black, others are gray or just an off-white color. Sometimes the discoloration is so faint that it is only visible when the ceramic tube is viewed from the side through the glass. A gradual change from white on the inside to off-white or gray on the outside can be seen. Silver sulfide makes the diaphragm appear black. Proteins can cause a whitish discoloration that is hardly visible. This form of contamination rarely occurs just on the surface. It usually penetrates into the pores of the diaphragm. Lipophilic substances, such as fats and oils, can create a thin, non-permeable layer over the diaphragm that is often invisible.

In general, three procedures can be followed to restore an electrode to its normal working state. First of all, the glass membrane can be regenerated, secondly, the reference diaphragm may have to be cleaned and thirdly, it may be necessary to replace the electrolyte. This latter point will not be discussed in this article because it forms part of the normal electrode maintenance procedure.

---

**Figure 1:** What can be fixed?

**Figure 2:** Regeneration Procedure
**Tips and Tricks**

Cleaning procedures

The following table gives tips and hints on how to clean ceramic diaphragms. Some of these measures can be used on the outside as well as on the inside of the electrode. The same applies of course to Redox or separate reference electrodes which have a contaminated ceramic diaphragm.

<table>
<thead>
<tr>
<th>Type of contamination</th>
<th>Cleaning agent</th>
<th>Reaction time</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver sulfide</td>
<td>Thiourea ME-51340070</td>
<td>5 – 60 mins.</td>
<td>Leave until discoloration disappears.</td>
</tr>
<tr>
<td>All possible types of contamination. First</td>
<td>HCl 0.1 mol/L</td>
<td>Approx. 12 hrs.</td>
<td>Can also be used for internal cleaning.</td>
</tr>
<tr>
<td>recommendation for removing unknown substances.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All possible types of contamination. Second</td>
<td>Chromic-sulfuric acid mixture</td>
<td>Approx. 30 mins.</td>
<td>Also cleans deposits on the membrane very well. <strong>Sensor must be regenerated after this procedure.</strong></td>
</tr>
<tr>
<td>recommendation for removing unknown substances.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proteins</td>
<td>Pepsin / HCl cleaning solution ME-51340068</td>
<td>&gt; 1 hr.</td>
<td></td>
</tr>
<tr>
<td>Proteins</td>
<td>NaOH 2%</td>
<td>Approx. 20 mins.</td>
<td></td>
</tr>
<tr>
<td>Lipophilic substances</td>
<td>Ethanol, acetone</td>
<td>Approx. 30 mins.</td>
<td>Highly suitable for edible oils. Possibly with support of a soft brush.</td>
</tr>
<tr>
<td>Calcium, scale</td>
<td>Acetic acid</td>
<td>Approx. 30 mins.</td>
<td><strong>Sensor must be regenerated after this procedure.</strong></td>
</tr>
<tr>
<td>Soaps, tensides</td>
<td>Hot water (80° C)</td>
<td>Approx. 12 hrs.</td>
<td>Rinse sensor well with hot water. Afterwards, immerse in hot water and leave to cool, approximately 12 hours. Only use tap water, not distilled or de-ionised water.</td>
</tr>
</tbody>
</table>

Table 2: Clogged Reference Diaphragm: Causes and Cleaning Procedures

Special notes for InLab® electrodes:
- Since InLab® electrodes can be used for field measurements in conjunction with portable meters, these electrodes are very often submerged in the sample. MultiPin and S7 are not rated according to ingress protection IP67. This is a problem particularly when the sample contains salt, which enhances corrosion. Always check the connectors for signs of corrosion when the electrode has been submerged.
- Gel-filled InLab® sensors, e.g. InLab® 417, should not be stored horizontally. Bubbles that form around the lead-off elements and in the tip of the electrode cause erroneous readings. However, since the gel is highly viscous, the bubbles cannot be removed by shaking. Always store such electrodes vertically, with the tip of the electrode facing downward.

Despite all the corrective procedures mentioned above, it is not always possible to repair a faulty electrode. Damage that has occurred to the wiring or casing of an electrode during use, is irreparable. In such cases the electrode must be replaced.
Titration applications on the internet:

...fast, up-to-date and free!

METTLER TOLEDO titration literature contains a wide range of well-proven applications. Most of this information can now be downloaded directly from the Internet or, as previously, ordered as individual brochures.

The internet offers several advantages compared with ordering hardcopies. By typing in a keyword, you can search for specific applications very quickly; by choosing an industry, all the relevant applications are displayed together. And because the application database is constantly being updated, the user is always sure that he has the very latest information. By the time this UserCom goes to press, the application database will contain well over 200 applications, including all the applications in the DL5x and DL7x titrator brochures.

The step-by-step description below explains how to use the application database. All you need is a computer with Internet access and a Web browser like the Microsoft Internet Explorer or Netscape Navigator.

How to navigate to the application database

1. Direct your internet browser to “www.titration.net” and click on any picture on the page. The titration main page appears. Click “Applications”.

2. On the “Applications” page, click “Find your application”.

3. The database input form appears. Bookmark it for later use (click “Add to Favorites” in the Internet Explorer)
Tips and Tricks

How to use the database

1. Type the name of the topic, substance or material you are looking for in the keyword box. You can combine/limit your search by selecting an industry from the pull-down menu and linking it with “and/or” logical operators.

2. A list of search results including a short summary appears. Select the application you want to see in detail by clicking its title. You are requested to enter your username and password. If you are not yet registered on titration.net, you can do this by clicking “register”.

3. The application screen contains all the information in the application brochures (except the curves). You can print it out if required.
The application chemists of the AnaChem market support group have prepared several publications and a series of application brochures to support customers in their routine work in the laboratory. Each brochure is dedicated either to a particular branch of industry (such as paper and pulp, petroleum and beverages), a particular titrator or a specific analysis technique. The following list shows all the publications together with their order numbers. They are available from your local METTLER TOLEDO marketing organization.

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* Also available in French (51709856), Spanish (51709857) and Italian (51709858)