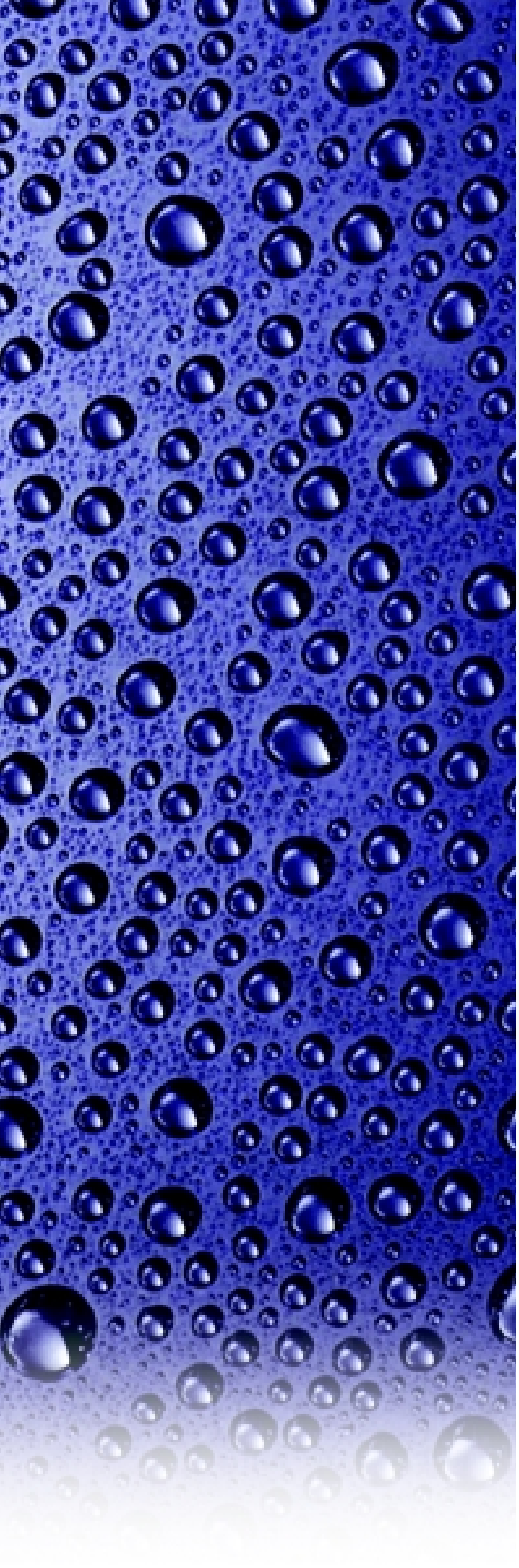
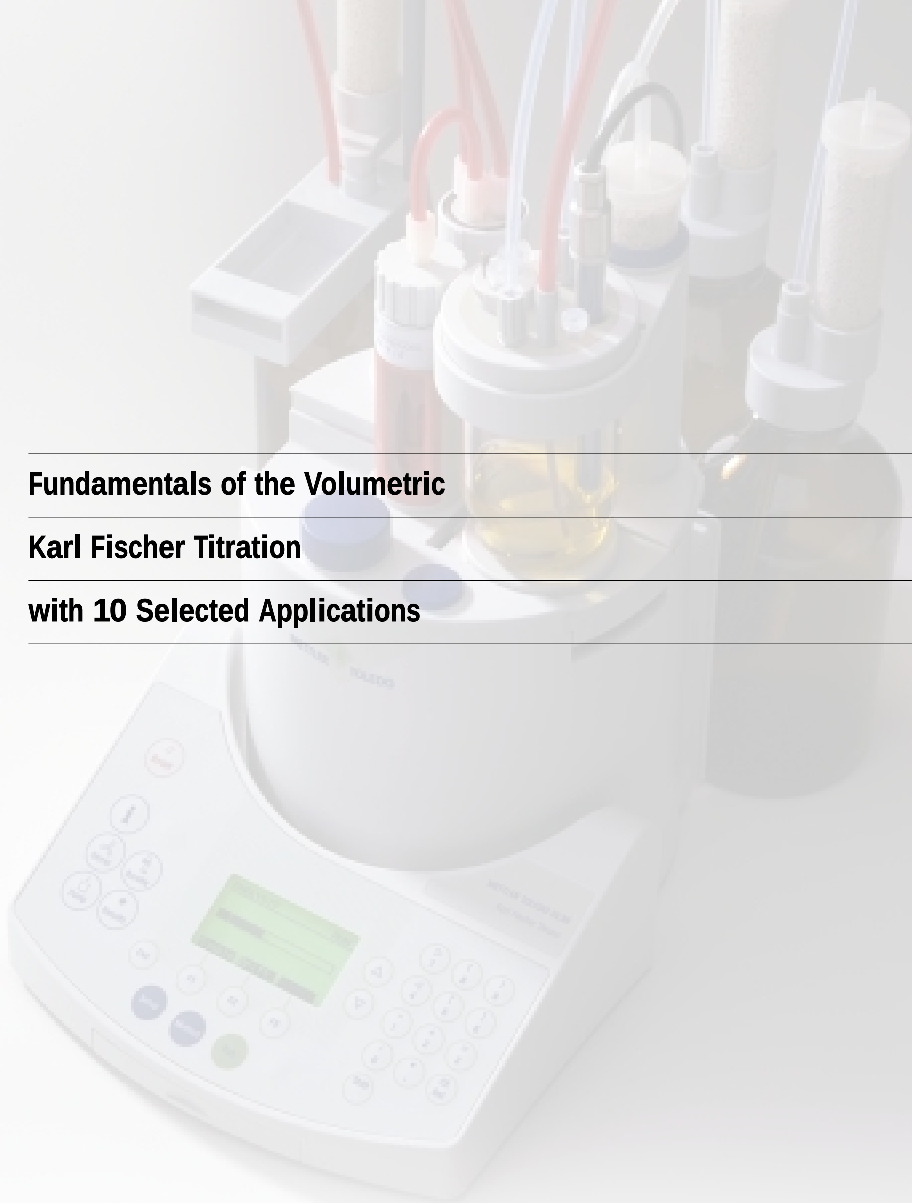




## Fundamentals of the Volumetric
## Karl Fischer Titration
## with 10 Selected Applications

# METTLER TOLEDO DL31/DL38 Titrators

Application brochure 26

METTLER TOLEDO

# Editorial

Dear Reader

A new instrument for Karl Fischer titration is born. The DL31 and DL38 titrators differ not only in appearance from conventional instruments. Significant improvements have been made in the important fields of accuracy, precision, speed, GLP compliant documentation, and user-friendliness. It is extremely important for us that our users can take full advantage of these new possibilities.

With this goal in mind, in the usual METTLER TOLEDO tradition, we have prepared this applications brochure. Included are explanations and hints for titrant concentration determination, analysis of solid samples using a drying oven, external extraction or with the aid of an homogenizer. A detailed description of moisture determination in gases is also given. Until now this information has been difficult to come by.

In this brochure we go one step further. The Karl Fischer titration is explained in terms of the chemistry as well as control of the titration. Practical tips are given on sample preparation, handling of the instrument in a humid environment, as well as tips on optimizing accuracy and precision of the method.

This information was collected, arranged and developed by the long-time applications chemist, Albert Aichert. With 25 years laboratory experience, of which approximately 20 years were in a development laboratory of a large chemical concern, he has the experience to provide much valuable input. Tips from an analyst for the analyst. The most important is that you, as the user, have the possibility of using a METTLER TOLEDO titrator to its full potential.

We wish the greatest success but also enjoyment.

C Walter

R. Rohner

Christian Walter
Manager Market Support AnaChem

Rolf Rohner
Marketing Manager Titration

# Contents

Page

Page

Page

# 1 The Karl Fischer reaction

The determination of the water content is based on the reaction described by R. W. Bunsen [1]:

$$I_2 + SO_2 + 2\,H_2O \longrightarrow 2\,HI + H_2SO_4$$

Karl Fischer [2] discovered that this reaction could be used for water determinations in a non-aqueous system containing an excess of sulfur dioxide. Methanol proved to be suitable as a solvent. In order to achieve an equilibrium shift to the right, it is necessary to neutralize the acids that are formed during the process (HI and $H_2SO_4$). Karl Fischer used pyridine for this purpose.
Smith, Bryanz and Mitchell [3] formulated a two-step reaction:

$$I_2 + SO_2 + 3\,Py + H_2O \longrightarrow 2\,Py\text{-}H^+I^{\text{Ð}} + Py\text{¥}SO_3$$
$$Py\text{¥}SO_3 + CH_3OH \longrightarrow Py\text{-}H^+CH_3SO_4^{\text{Ð}}$$

According to these equations, methanol not only acts as a solvent but also participates directly in the reaction itself. In an alcoholic solution, the reaction between iodine and water takes place in the stoichiometric ratio of 1:1.
In an alcohol-free solution, the reaction between iodine and water takes place in the stoichiometric ratio of 1:2:

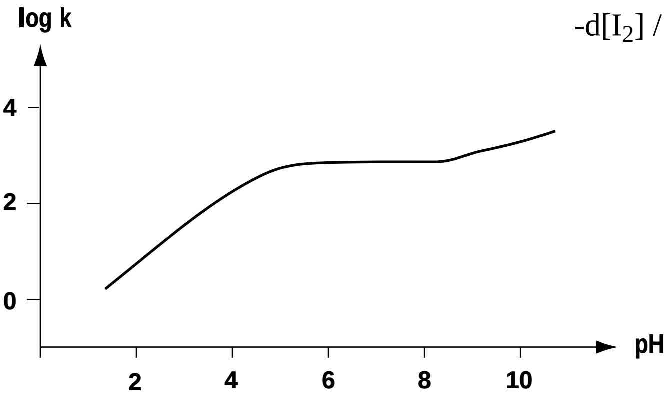
$$I_2 + SO_2 + 3\,Py + \mathbf{H_2O} \longrightarrow 2\,Py\text{-}H^+I^{\text{Ð}} + Py\text{¥}SO_3$$
$$Py\text{¥}SO_3 + \mathbf{H_2O} \longrightarrow Py\text{-}H^+HSO_4^{\text{Ð}}$$

Further studies conducted by E. Barenrecht and J. C. Verhoff [4] on the subject of the Karl Fischer reaction have revealed that

¥ Pyridine is not directly involved in the reaction, i.e., it only acts as a buffering agent and can therefore be replaced by other bases,

¥ the rate of the Karl Fischer reaction depends on the pH value of the medium (see graph):

$$-d[I_2] / dt = k\,[I_2]\ \text{¥}\ [SO_2]\ \text{¥}\ [H_2O]$$



One explanation for this relationship between the pH value and the reaction rate is that it is not the sulfur dioxide itself that is oxidized by iodine under the influence of water, but rather the methyl sulfite ion, which is formed from sulfur dioxide and methanol:

$$2\,CH_3OH + SO_2 \longrightarrow CH_3OH_2^+ + CH_3OSO_2^{\text{Ð}}$$

The higher the pH value of the solution, the more methyl sulfite is formed by the capture of protons and the faster the Karl Fischer reaction.

In the pH range from 5.5 to 8, all of the sulfur dioxide is available as methyl sulfite: the maximum reaction rate is reached here. Due to the side reactions between iodine and hydroxide or methylate ions, the rate rises again at pH values greater than 8.5; this results in a vanishing end point and a higher iodine consumption during the titration.

## 1.2 Recent research into the reaction sequence

In 1984 E. Scholz [5] developed a pyridine-free Karl Fischer reagent with imidazole as base. This reagent not only replaced the toxic, pungent pyridine, but also facilitated faster, more accurate titration, as imidazole buffers in a more favorable pH range than pyridine. The stoichiometric analyses carried out by E. Scholz also revealed that other alcohols capable of improving the titer stability of the reagent, such as ethanol, 2-propanol or methoxyethanol, can be substituted for methanol. These findings yielded the following equation for the Karl Fischer reaction:

$$\mathrm{ROH} + \mathrm{SO_2} + \mathrm{RN} \longrightarrow \mathrm{(RNH)\cdot SO_3R}$$

$$\mathrm{(RNH)\cdot SO_3R} + \mathrm{I_2} + \mathbf{H_2O} \longrightarrow \mathrm{(RNH)\cdot SO_4R} + 2\,\mathrm{(RNH)I}$$

E. Scholz was also able to confirm the existence of basic methyl sulfite in methanol/$SO_2$/$I_2$ solutions during the titration. In 1988 A. Seubert [6] detected methyl sulfite in KF solutions with the aid of IR spectroscopy and isolated and identified di-methyl sulfate as a secondary product of the KF reaction.

Recent studies have postulated that the oxidizing molecules are not $I_2$ or $RN\cdot I_2$, but rather that part of the $I_2$ in the polar solvents reacts disproportionately to form $I^-$ and $RNI^+$ and that the $RNI^+$ then reacts further.

## 1.3 Consequences for practical applications

*pH dependance of the Karl Fischer reaction*

Since the maximum speed of the Karl Fischer titration is reached in the pH range from 5.5 to 8, you should avoid pH values greater than 8 and less than 4 in practice. With acidic or basic samples you should adjust the pH of the titration solution by the addition of buffering agents (with imidazole as the basic buffer and salicylic acid as the acid buffer).

*Effect of the solvent on the Karl Fischer reaction*

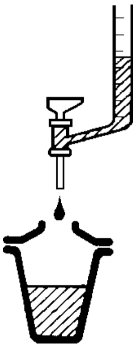
The stoichoimetry (molar ratio $H_2O:I_2$) depends on the type of solvent (see Section 1). Investigations by Eberius [7] have shown that iodine and water react in the ratio of 1:1 if the percentage of methanol in the solvent is 20% or more. Methanol should therefore always be present in the minimum required amount. If you need to use a methanol-free titrant (for ketones and aldehydes), you can also use other primary alcohols.

*Effect of the amount of water on the Karl Fischer reaction*

The molar ratio $H_2O:I_2$ is also influenced by the amount of water in the sample. J. C. Verhoff and E. Barenrecht [4] observed a rise in the titer with water contents greater than 1 mol/L. This, however, is of no consequence for practical applications, because the water concentration in the solvent is significantly lower.

# 2 Reagents

## 2.1 One-component reagent



The **titrant** contains iodine, sulfur dioxide and imidazole, dissolved in a suitable alcohol.

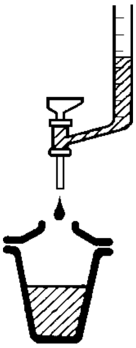
The **solvent** is methanol.

You can also use a methanolic solvent mixture specially adapted to the sample as the solvent.

The reagent can be stored for approximately two years. The drop in titer, i.e., the decrease in concentration, is 0.5 mg/mL per year in a sealed bottle.
The reagent is available in three different concentrations:

- 5 mg/mL for samples with a water content of 1000 ppm to 100%,
- 2 mg/mL for samples with a water content of less than 1000 ppm,
- 1 mg/mL for samples with a water content of less than 200 ppm.

## 2.2 Two-component reagent



The **titrant** contains iodine and methanol.

The **solvent** contains sulfur dioxide, imidazole and methanol.

A titration speed two or three times as high can be achieved with the two-component reagent. Both the components are extremely stable in storage.

The titrant has a stable titer, provided that the bottle is tightly sealed. It is available in two different concentrations:

- 5 mg/ mL for samples with a water content of 1000 ppm to 100%,
- 2 mg/ mL for samples with a water content of less than 1000 ppm.

| **Comparison of reagents** | + | – |
|---|---|---|
| One-component | Simple handling,<br>favorably priced. | Titer less stable,<br>titration speed slower. |
| Two-component | High titration speed,<br>stable titer. | Solvent capacity<br>restricted. |

## 2.3 Pyridine-containing reagents

Despite the existence of pyridine-free reagents, which allow fast and accurate Karl Fischer titrations, reagents containing pyridine are still frequently used because they are cheaper and can be made in-house; pyridine-free reagents are not even available in some countries.

**One-component reagent:**

- The titrant contains iodine, sulfur dioxide and pyridine, dissolved in methanol,
- the solvent is either methanol or consists of methanol mixtures.

Some chemical manufacturers have increased the pyridine content of the titrant slightly to achieve a higher titration speed. This reagent is declared as "rapid". To obtain better stability, a number of manufacturers also sell the titrant separated into solution A and solution B. Solution A is sulfur dioxide and pyridine dissolved in methanol while solution B is iodine dissolved in methanol. These solutions are mixed 1:1 before they are used, to form the one-component titrant.

**Two-component reagent:**

- The titrant contains iodine, dissolved in methanol,
- the solvent contains sulfur dioxide and pyridine, dissolved in methanol.

Separating the two components results in excellent stability in storage and a higher titration speed.

## 2.4 Special reagents for aldehydes and ketones

In combination with the standard methanol-containing reagents, aldehydes and ketones form acetals and ketals. Water is produced and titrated at the same time, resulting in falsified water contents and a vanishing end point. Special methanol-free, one-component reagents (Riedel-de Ha‘n, Fluka) and a two-component reagent (MERCK) are available on the market to prevent this problem.

**One-component reagent:**

- The titrant contains iodine, imidazole, sulfur dioxide and 2-methoxyethanol,
- the solvent contains 2-chloroethanol and trichloromethane.

The titration takes slightly longer with the special one-component reagent for aldehydes and ketones than with the ordinary one-component reagent. The special reagent is also suitable for other substances that react with methanol, such as amines.

## 2.5 Karl Fischer reagents with ethanol

Since ethanol is less toxic than methanol, Riedel-de Ha‘n launched ethanol-based Karl Fischer reagents on the market in 1998. These reagents allow titration of several ketones which form ketals considerably slower in ethanol than in methanol.

A special, ethanol-based solvent is available for the **one-component reagent**.

**Two component reagent:**

- The titrant contains iodine and ethanol,
- the solvent contains sulfur dioxide, imidazole, di-ethanolamine and ethanol.

# 3 Control

The addition of titrant during the Karl Fischer titration must be controlled, just as with any other titration method: Ideally, the titrant should be added as quickly as possible and the addition stopped exactly at the end point. This is the only way to determine the titrant consumption precisely.

Control is only possible if the end point is indicated. The titration speed depends on four different factors:

¥ The reaction rate between the titrant and the sample,

¥ the stirring rate and mixing of the titrant,

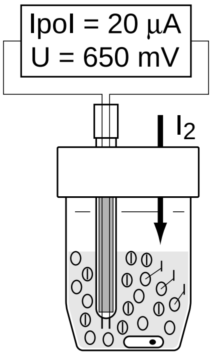
¥ the control algorithm and the control parameters,

¥ the termination of the titration.

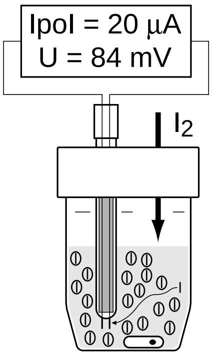
## 3.1 Indication

### 3.1.1 Principle of bivoltametric indication

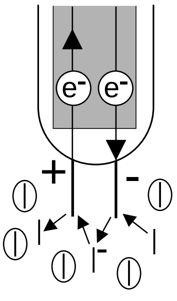
A bivoltametric indication is used for the Karl Fischer titration. A small, constant current Ð the polarization current "Ipol" Ð is applied to a double platinum pin electrode.



As long as the added iodine reacts with the water, there is no free iodine in the titrating solution. A high voltage is necessary to maintain the specified polarization current at the electrode.



As soon as all the water has reacted with iodine, there will be free iodine in the titration solution. This free iodine causes ionic conduction and the voltage needs to be reduced to keep the polarization current constant. When the voltage drops below a defined value, the titration is terminated.



The ionic conduction takes the following course: an iodine molecule is attracted to the negatively charged platinum pin. It then acquires two electrons and turns to iodide (2 $\mathrm{I}^{Ð}$). The two negatively charged iodide ions are immediately attracted to the positively charged platinum pin, where they donate the electrons and form an iodine molecule again.

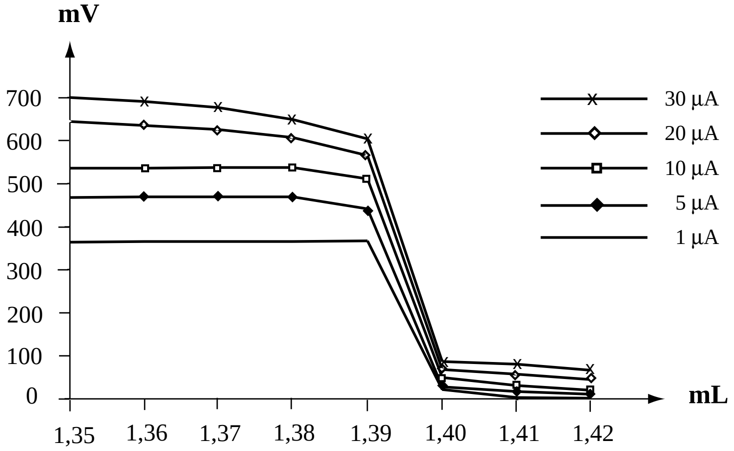
The titration solution must be mixed thoroughly to ensure constant ionic conduction (see Section 3.3).

### 3.1.2 End point and polarization current

The Karl Fischer titration is terminated when free iodine is detected in the titration solution, i.e., the titration end point is reached when the potential at the polarized, double platinum pin electrode drops below a defined value. This value depends, above all, on the polarization current and to a lesser extent on the type of electrode as well as on the solvent that is used.

The following end points have been defined for reagents containing methanol (with double platinum pin electrode, pin length: 3 to 4 mm, pin diameter: 1 mm):

| Ipol | End point |
|---|---|
| 1 µA | 20 to 30 mV |
| 5 µA | 50 to 70 mV |
| 10 µA | 80 to 100 mV |
| 20 µA | 100 to 120 mV |
| 30 µA | 130 to 150 mV |
| 40 µA | 150 to 170 mV |



Notes

1. You can use the same end points for ethanol-based reagents.
2. You should use end points roughly 20% higher for reagents for aldehydes and ketones, where the methanol has been replaced by 2-methoxyethanol.

*Influence of the electrode*

The potential jump at the end of the titration is also influenced by the electrode:

Ð Electrodes with a large platinum surface, e.g. with longer pins, a double ring or plates instead of pins, result in a smaller potential jump and a lower end point. The larger the platinum surface, the smaller the potential jump. Double-ring electrodes, for example, have an initial potential of approx. 350 mV and an end point at approx. 40 mV with 20 µA.

Ð Electrodes with very short platinum pins (< 3 mm), on the other hand, cause a larger potential jump and a higher end point. A 2 mm long pin, for example, causes an initial potential of approx. 750 mV and an end point at approx. 140 mV with 20 µA.

## 3.2 Reaction rate

The reaction rate depends on

¥ the water concentration,

¥ the sulfur dioxide concentration,

¥ the iodine concentration,

¥ the pH value of the solution (see Section 1).

This has the following consequences for the titration:
Initially, when the water content is high, the titrant can be added quickly since the iodine reacts with the water immediatly. Towards the end of the titration, when the water content is lower, the reaction rate decreases and the titrant must be added more slowly, because there is only a small amount of water left to react with the iodine.

- With the one-component reagent, the sulfur dioxide required for the reaction is added in slight excess with the iodine solution.
- With the two-component reagent, sulfur dioxide is present in large excess in the solvent.

The difference in the sulfur dioxide concentration results in a reaction rate that is 2 to 4 times faster for the two-component reagent than for the one-component reagent. Karl Fischer titrations with the two-component reagent are thus significantly quicker than with the one-component reagent.

Example of titration times with:

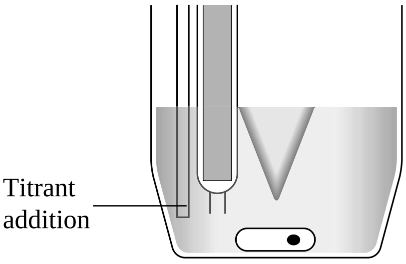
| | |
|---|---|
| One-component reagent: | 110 to 140 seconds with a titrant consumption of 2.5 mL, |
| Two-component reagent: | 45 to 55 seconds with a titrant consumption of 2.5 mL. |

## 3.3 Stirring speed and dispersion of the titrant

Good mixing is essential for fast, accurate Karl Fischer titrations. Mixing is influenced by the following factors:

¥ The stirring speed,
¥ the point of titrant addition,
¥ the shape of the vessel.

### 3.3.1 Stirring speed

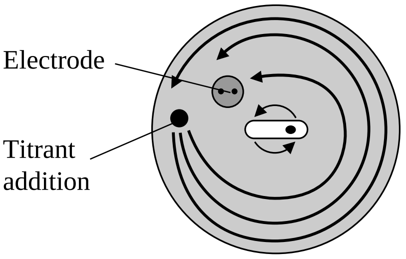


The optimum stirring speed is obtained when a small vortex is visible (see diagram).

If the stirring speed is too slow, the titration may also be too slow and irregular, and overtitration may occur.

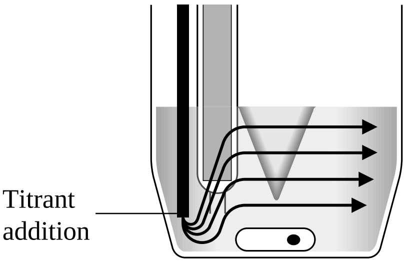
If bubbles form in the solution, the stirring speed is too fast. Bubbles falsify the measured values.

### 3.3.2 Point of titrant addition



The titrant should be added where the turbulence is greatest; the point of addition should be sufficiently far away from the electrode to allow the iodine sufficient time to react.
If the titrant is added too close to the electrode, the latter may detect non-reacted iodine, with the result that the titrant is added more slowly and the titration time increases.

### 3.3.3 Vessel shape



The conical shape of the titration beaker and the short stirring bar* produce strong turbulence in the zone surrounding the point of titrant addition, so that the titrant is dispersed effectively. This is essential for a fast reaction rate and thus also for short titration times.

* If a longer stirring bar is used, there would be no more turbulence and the mixing quality would be poorer. The added iodine would moreover not be distributed upwards, but rather along the base directly towards the electrode.

## 3.4 Control of the titration

The Karl Fischer titration is a continuous end point titration.

Ð With the conventional continuous end point titration, the titrant addition rate is proportional to the **distance from the end point**; the closer the end point, the slower the titrant is added. The proportionality is determined by the control range (control band).

Ð When **DL31/DL38 titrators** are used for continuous end point titration, the titrant addition is controlled by a fuzzy logic algorithm. The rate of titrant addition depends on the **distance from the end point** and on the **potential change** with each addition. The titration is adapted to the titration curve, i.e., even though the titrant is added faster, the addition can still be stopped exactly at the end point. This results in shorter titration times and extremely accurate results.

### 3.4.1 Principle of fuzzy logic control

The difference between continuous end point titration with conventional or fuzzy logic control can be explained with the following example:

A train travels to a station at which it has to stop. The braking phase needs to be optimized Ð not too soon or the journey will take too long and not too late or the train will be braked too abruptly, which will not please the passengers.

- If the railway line runs over very flat terrain, the braking phase can always be started the same distance away from the station. This is an easy matter for the "conventional" train driver, who always applies the brake 300 m before reaching the station: this ensures the optimum brake reaction in terms of both time and comfort. (In the titration context the control range for conventional control always starts at 300 mV).
- If the railway line crosses hilly terrain, the start of the braking phase will be different:
  ¥ The steeper the gradient down to the station, the sooner the train driver must apply the brake,
  ¥ the steeper the gradient up to the station, the later the train driver must apply the brake.

  The start of the braking phase thus differs from one station to the next. The "conventional" train driver, who does not take any account of the terrain, needs exact distance information for every station in order to optimize the start of the braking phase in terms of time and comfort. (In the titration context the control range for conventional control must be adapted individually to every sample matrix in order to optimize the addition of the titrant).
- The "fuzzy logic" train driver does not require any additional information, because he pays attention to both the terrain and the distance from the station and automatically starts the braking phase at the right time. (In the titration context the fuzzy logic control range does not need to be adapted).

## 3.5 Termination of the titration

The KF titration can be terminated using various parameters. Since the "first" KF reagents reacted slowly, a delayed switch-off time of 10 to 20 seconds was set at the end point. It has since been possible to reduce this delay time to 5 to 10 seconds, thanks to the development of

- new, pyridine-free reagents with a faster reaction rate,
- high-resolution burettes (0.1 to 0.5 µL),
- more tightly sealed titration stands.

In addition, the online determination of the drift during the titration has enabled a "drift stop" to be used as a termination parameter. This parameter shortens the titration time and leads to reproducible results (see Section 4.2).

# 4 DL31/DL38: Control and termination parameters

## 4.1 Control parameters

### 4.1.1 ∆Vmin and ∆Vmax

The end point titration is controlled with an addition interval of 0.1 seconds. The basic control parameters are

- **∆Vmin** = smallest addition increment in µL per 0.1 seconds,
- **∆Vmax** = largest addition increment in µL per 0.1 seconds.

The ∆Vmax and ∆Vmin limits depend on the burette volume. The burette has a resolution of 10 000 steps. Up to 40 steps are possible in 0.1 seconds. The limits for the two control parameters are thus as follows:

| **Burette volume** | **∆Vmin** | **∆Vmax** |
|---|---|---|
| 1 mL | 0.1 µL | 4 µL |
| 5 mL | 0.5 µL | 20 µL |
| 10 mL | 1.0 µL | 40 µL |
| 20 mL | 2.0 µL | 80 µL |

How to choose the optimum control parameters is described in Section 4.4.2.

### 4.1.2 ∆Vmax factor

The reaction rate for the two-component reagent is extremely fast. It is therefore possible to titrate with a large ∆Vmax to obtain short titration times. A large ∆Vmax at the end of the titration however, can lead to overtitration. The ∆Vmax factor causes ∆Vmax to be reduced shortly before the end of the titration and thus prevents overtitration.

∆Vmax factor = **∆Vmax reduction to 1 – 100%**

This factor allows 97 to 99% of the titrant to be added very quickly, taking advantage of the fast reaction rate while the titration end point is reached exactly by adding small increments.

*Example of the titration of methanol*

| 5 samples: mean value = 6132 ppm, relative standard deviation = 0.06% | | | |
|---|---|---|---|
| Titrant consumption [mL] | 0.9 | 1.7 | 2.4 |
| Titration time [s] | 26 | 43 | 55 |

How to choose the optimum factor is described in Section 4.4.3.

### 4.1.3 Cautious start

An end point titration controlled using fuzzy logic is extremely rapid. If the water content is very low, the titration starts so quickly that overtitration may occur. In this case you can activate the **Start: Cautious** parameter. The titrator then begins with the smallest increment ΔVmin and increases it linearly to ΔVmax within 20 seconds.

Notes

1. You should always select **Start: Cautious** for one and two-component reagents if the amount of water in the sample is less than 100 µg.
2. You can also set ΔVmax to a lower value for small amounts of water if you wish the titration to progress more cautiously, e.g. ΔVmax = 2 µL. With large amounts of water, however, the titration will take too long. The **cautious start** allows the same parameters to be used regardless of the amount of water.
3. The DL31/38 titrators always use the cautious start for pretitration, to ensure that no overtitration occurs even if the water content is very low (solvent almost completely titrated).

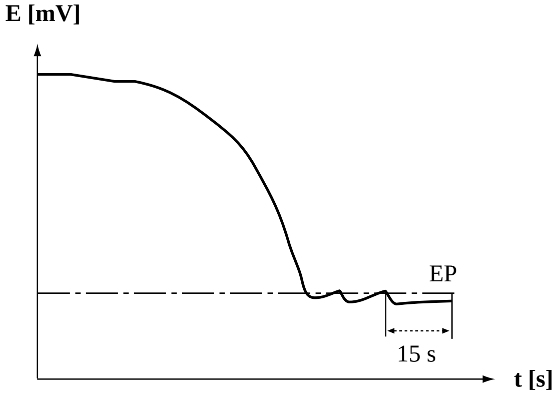
## 4.2 Termination parameters

The DL31/38 titrators have four termination parameters:

- Delay time,
- Absolute drift stop,
- Relative drift stop,
- Maximum titration time.

The additional "maximum volume" parameter of the titrators is a safety parameter and is therefore not considered to be a termination parameter.

### 4.2.1 Delay time

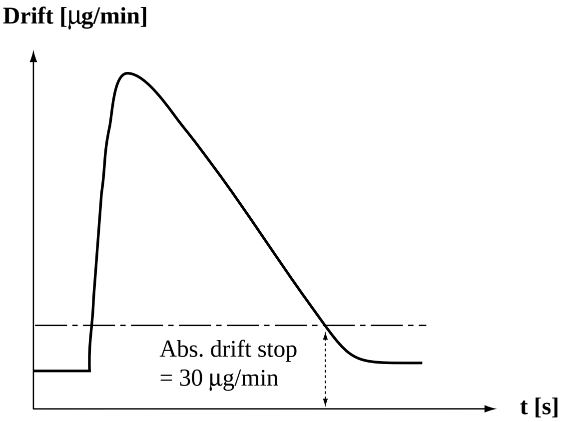


The titration is terminated when the potential remains below the end point for a defined time (e.g. 15 s) following the addition of a titrant increment. The smallest increment ΔVmin must be sufficiently large to compensate the drift (see Section 4.4.2).

Typical delay time: 15 seconds

**Disadvantage**: ΔVmin must be adapted to the initial drift and the titrant concentration.

### 4.2.2 Absolute drift stop

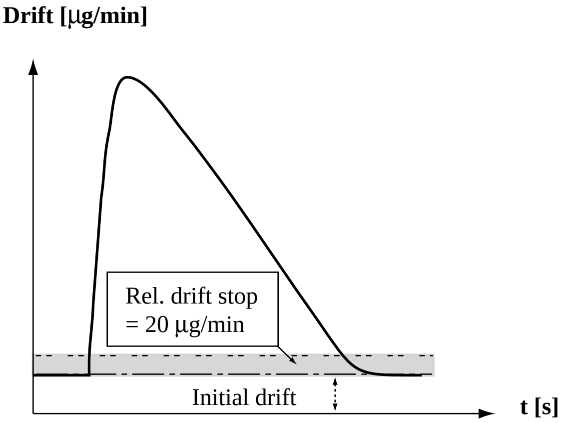


The titration is terminated when the actual drift is less than the predefined absolute drift value. The value of the absolute drift stop must be greater than the initial drift, or the termination criterion will never be satisfied and the titration will continue indefinitely.

Typical absolute drift stop value = 30 µg/min

**Advantage**: Independent of the titrant concentration.
**Disadvantage**: The value of the absolute drift stop must take account of the initial drift.

### 4.2.3 Relative drift stop



The titration is terminated when the actual drift is less than the sum of the initial drift and the relative drift.

Typical relative drift stop value = 20 µg/min

**Advantage**: Independent of the initial drift and the titrant concentration.

### 4.2.4 Maximum titration time

The titration is terminated after the defined time.

How to use and optimize the termination parameters is described in Section 4.4.5.

## 4.3 Default control and termination parameters

Titrant-specific control and termination parameters are stored in the DL31/DL38 titrators. They are intended to help you find the "right" control parameters quickly and easily. The KF standard method, the Tutorial, the learn titration and the METTLER methods are also useful in this connection.

### 4.3.1 KF standard method and Tutorial

Control and termination parameters are optimized for samples with straightforward matrices and stored for the "one and two-component reagent" and "pyridine-containing, one-component reagent" **titrant types**:

| Titrant type | Ipol µA | EP mV | ΔVmin µL | ΔVmax µL | ΔVmax factor % | Rel. drift stop µg/min |
|---|---|---|---|---|---|---|
| One-component | 20 | 100 | 0.5 | 4.0 | 100 | 15 |
| Two-component | 20 | 100 | 0.5 | 8.0 | 30 | 15 |
| Pyridine-cont. (one-comp.) | 20 | 100 | 0.5 | 3.0 | 100 | 15 |

Note
You must select "1-component", "2-components", "Pyridine" or "Others" as the titrant type in the titrant parameter list. If you choose "Others", the parameters for the one-component reagent are adopted (see DL31/DL38 Operating Instructions, Section 4.1).

The appropriate titrant-specific parameter values are **automatically loaded** for the titrant you select when you develop a method using the KF standard method or the Tutorial. If these control parameters do not produce an optimum titration, they can be changed (see Section 4.4).

### 4.3.2 Learn titration

The learn titration needs only four inputs to titrate a sample:

- Method number,
- type of sample,
- result unit,
- titrant (type).

Control and termination parameters are calculated based on the titrant type and the titration progress. At the end of the learn titration, the following results are given:

- Water content of the sample in the selected unit,
- optimized control and termination parameters: ΔVmin, ΔVmax, ΔVmax factor and relative drift stop,
- limit values for the amount of sample.

These "learnt" parameters are stored as a user method under the defined number.

If the learn titration is unable to find an end point, the titration is terminated either after two burette volumes have been added or after 10 minutes; a method with control and termination parameters is still developed based on the titrant type.

### 4.3.3 METTLER methods

Eight optimized Karl Fischer methods for various applications are stored in the DL38 titrator (see page 52).

You can use these methods directly, providing you are working with the one-component reagent. If you are using a two-component reagent or one containing pyridine, you must adapt the control and termination parameters to the titrant in order to optimize the determinations.

## 4.4 Optimizing the control and termination parameters

### 4.4.1 Polarization current and end point

Each end point is valid for a specific polarization current, i.e., if the polarization current changes, the endpoint must be adjusted (see table in Section 3.1.2).

*Polarization current*

You can reduce the titration time by increasing the polarization current.
Example for a one-component reagent with a titrant consumption of 0.5 mL:

| Polarization current [µA] | 5 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Titration time [min] | 3:05 | 2:17 | 1:41 | 1:22 | 1:23 |

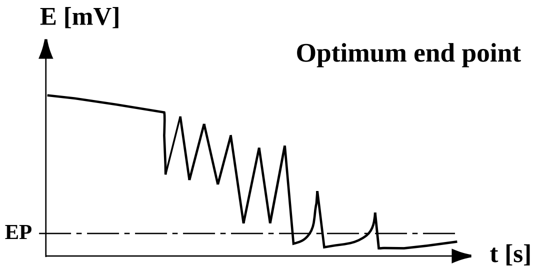
The greatest time saving can be achieved by increasing the current from 5 to 20 µA; a further increase to 30 or 40 µA does not bring any significant improvement. However, the higher polarization current causes the electrode to become contaminated sooner (the higher electrode polarity attracts more "dirt"). A polarization current of 20 µA has therefore been chosen as default.

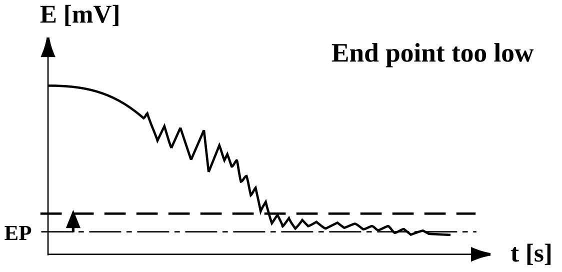
*End point*

The end point for a specific polarization current is influenced by the electrode and the solvent. In particular, selecting a higher end point results in longer titration times and poorer reproducibility. The following are possible contributing factors:

- Contaminated or old electrodes,
- electrodes with very short platinum pins (< 3 mm),
- higher alcohols, e.g. isopropanol, used as solvent instead of methanol or ethanol.

The consequences of choosing an end point that is too low can best be demonstrated with the aid of the potential/time curve:





The titration curve is more or less flat towards the end; this results in an ill-defined titration end point.

### 4.4.2 ΔVmin and ΔVmax

*ΔVmin*

You should always use as small an increment as possible. This value depends on the burette volume (see Section 4.1.1). An exception is if you have selected "delay time" as a termination parameter in conjunction with a high drift value. In this case, e.g., enter 3 µL for ΔVmin if

- the titrant concentration = 5 mg/mL,
- the drift = 35 µg/min,
- the delay time = 15 s.

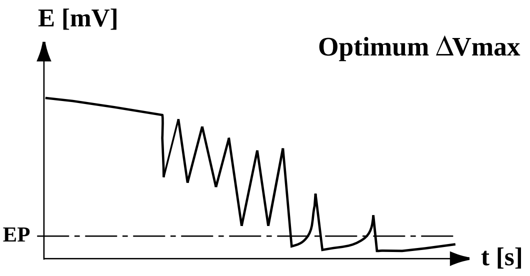
This is the only way to make sure that, at the end of the titration, one increment is sufficient to compensate the drift for a period of 15 seconds and thus terminate the titration. A lower ΔVmin will cause the titration to continue indefinitely.

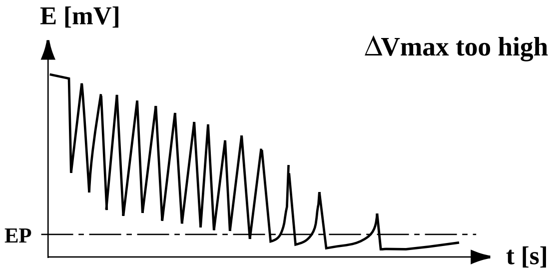
*ΔVmax*

You must adapt the largest addition increment to the titrant:

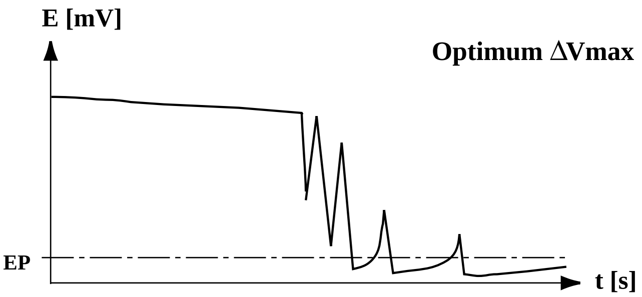
| Titrant for | ΔVmax |
|---|---|
| One-component reagent | 3.5 Ð 6µL |
| One-component reagent for ketones | 4 Ð 5µL |
| One-component reagent (pyridine-containing) | 3 Ð 4µL |
| Two-component reagent | 8 Ð 12µL |
| Two-component reagent (pyridine-containing) | 5 Ð 6µL |

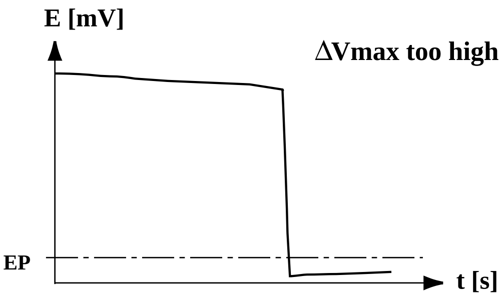
**One-component reagent**: You can optimize ΔVmax according to the titration time. If the value of ΔVmax is too high or too low, the titration time will be longer. If ΔVmax is too high, the iodine will be added faster than the reaction rate not long after the start of the titration. The addition will be interrupted repeatedly, so that the overall titration time is longer, even though the value of ΔVmax is relatively high.





**Two-component reagent**: If ΔVmax is too low, the titration time will be longer. A ΔVmax value that is too high will cause overtitration because the addition rate will be too fast. This will be evident from the potential/time curve.





### 4.4.3 ΔVmax factor

You should set this factor to 100% for all **one-component reagents**. The titration will otherwise take too long and its reproducibility will be less than perfect. Solvent mixtures containing formamide are an exception: they cause the reaction rate to increase to such an extent that the Karl Fischer reaction is almost as fast as with a two-component reagent. In this case you must set the factor to a value less than 100% (see next section).

You should set a factor of less than 100% for all **two-component reagents** (including those containing pyridine), to allow rapid, accurate determinations. The factor value depends on ΔVmax. Rule of thumb: the higher ΔVmax, the lower the ΔVmax factor.

Examples:

ΔVmax = 8.0 µL → ΔVmax factor = 30 - 40%
ΔVmax = 10.0 µL → ΔVmax factor = 25 - 35%
ΔVmax = 12.0 µL → ΔVmax factor = 20 - 30%

There is however an upper limit on ΔVmax to prevent overtitration (see Section 4.4.2).

### 4.4.4 Control parameters for various reagents

| **Reagents** | Ipol µA | EP mV | ΔVmin µL | ΔVmax µL | ΔVmax factor % | Rel. drift stop µg/min |
|---|---|---|---|---|---|---|
| One-component | 20 | 100 | 0.5 | 3.5 - 5 | 100 | 15 |
| One-component* | 20 | 100 | 0.5 | 5 - 6 | 100 | 30 |
| One-component (aldehydes & ketones) | 20 | 125 | 0.5 | 4 - 5 | 100 | 15 |
| One-component (methanol/formamide) | 20 | 100 | 0.5 | 6 - 8 | 50 - 35 | 15 |
| One-component (pyridine-containing) | 20 | 100 | 0.5 | 3 - 4 | 100 | 15 |
| Two-component | 20 | 100 | 0.5 | 8 - 10 | 30 - 25 | 15 |
| Two-component* | 20 | 100 | 0.5 | 11 - 12 | 25 | 30 |
| Two-component, ethanol-based | 20 | 100 | 0.5 | 5 - 6 | 40 - 35 | 15 |
| Two-component, ethanol-based* | 20 | 100 | 0.5 | 7 - 8 | 50 | 30 |
| Two-component (pyridine-containing) | 10 | 100 | 0.5 | 5 - 6 | 40 | 15 |

* Very fast titration with reduced accuracy; all the other options result in fast titrations with higher accuracy.

### 4.4.5 Using and optimizing the termination parameters

*Relative drift stop for unproblematic, soluble samples*

You should normally choose the relative drift stop as a termination parameter. This parameter is independent of the titrant concentration and the initial drift and is the most universal and easiest to use. The value of the relative drift stop influences the reproducibility and the titration time:

- Low drift stop value → better reproducibility → long titration time,
- High drift stop value → poorer reproducibility → short titration time.

One-component reagent
A relative drift stop of 10 to 15 µg/min is an optimum value for achieving good reproducibility.
A relative drift stop of 20 to 30 µg/min shortens the titration time, but involves a risk that the titration will be terminated a little too early, possibly resulting in poorer reproducibility and water contents that are too low. This is particularly critical in connection with the "slower" reagents for ketones and aldehydes.

Two-component reagent
A relative drift stop of 10 to 15 µg/min is an optimum value for achieving good reproducibility.
A relative drift stop of 20 to 40 µg/min shortens the titration time without affecting the reproducibility.

Insoluble samples (internal extraction)
The water contained in insoluble samples is extracted during the titration. The final traces are only extracted very slowly. If the water content is relatively high, you can ignore these traces, i.e., you can terminate the titration at a higher drift (relative drift stop = 40 to 70 µg/min). Use the drift/time curve to determine this value.

*Maximum titration time for samples whose water content is determined with the aid of the drying oven*

If the drying oven is used, the drift at the end of the titration is often greater than the initial drift. The reason for this is either that final traces of water are only released very slowly or that a thermal decomposition of the sample slowly takes place. The higher drift is therefore influenced to a large extent by the sample. With such samples, the best reproducibility is obtained with the maximum titration time (see also Section 7.5).

*Relative drift stop/maximum titration time for problematic samples*

With some samples there is a high drift value at the end of the titration. This is the case, for instance, with samples that only release the final traces of water very slowly or that produce side reactions. A combination of the relative drift stop and the maximum titration time has proved extremely effective for such samples. If the drift stop value is not reached, the titration is terminated at the latest after the defined maximum time.

# 5 Karl Fischer titration

Various factors must be taken into account with Karl Fischer titration to guarantee correct results:

¥ The atmospheric moisture,
¥ the titrant concentration,
¥ the solvent,
¥ the sample,
¥ the temperature,
¥ the side reactions between the sample and the Karl Fischer reagent.

## 5.1 Atmospheric moisture

Atmospheric moisture is the biggest single cause of error in Karl Fischer titrations. Moisture can enter the sample, the titrant and the titration stand. This problem is particularly common in tropical climates, where the relative humidity is more than 80%. The assumption that air-conditioned rooms have a lower atmospheric moisture is very often unfounded: the majority of air-conditioning systems simply cool the air. Since cold air can not absorb as much moisture however, the relative humidity increases. The higher the atmospheric moisture in the lab, the greater its influence on the results of the Karl Fischer titration. A Karl Fischer titrator should therefore never be installed directly in front of an air-conditioning system!

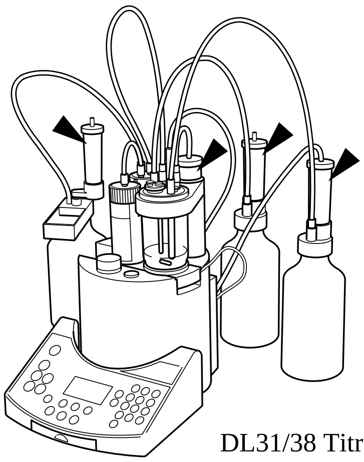
### 5.1.1 The titration stand

The titration stand must be sealed as tightly as possible against atmospheric moisture. It is necessary to observe the following rules:

1. Close all openings in the titration stand.
2. Condition the titration stand before using it:

   When you assemble the titration stand for the first time, there will be moisture on the glass surface of the titration vessel and on the built-in components; the air inside the titration vessel also contains moisture. After the solvent has been added, its water is titrated during pretitration. The drift value remains high however, because the moisture present on the glass wall and in the air inside the titration vessel migrates slowly into the solvent Ð it may take as long as 1 to 3 hours. You can cause the moisture to be titrated faster by shaking the titration vessel.

   **DL31/DL38**: These titrators have a stable drift value of less than 5 µg/min after just 15 to 20 minutes if their titration vessel is shaken three or four times (at intervals of 3 to 5 minutes).



DL31/38 Titrators

3. Protect the titration stand, the titrant, the solvent and waste bottles with a desiccant (molecular sieve with silica gel):

   The desiccant absorbs moisture and thus protects the titration stand against moisture ingress. Desiccants have a limited life: they are exhausted after 2 to 4 weeks, depending on the level of atmospheric moisture (the silica gel turns pink.) Silica gel can be regenerated at 150 °C and the molecular sieve at up to 300 °C.

### 5.1.2 The drift

No titration stand is completely water-tight; minute traces of water will always enter it. The total ingress of water into the titration stand during a defined period of time is referred to as **drift** and specified in µg $H_2O$/minute.

**DL31/DL38**: The titration stand of these titrators is exceptionally tight. The normal drift value is 1 to 3 µg $H_2O$/minute. The instruments indicate the drift value online during the standby titration. An arrow shows whether the value is stable, is drifting up or down. At the start of a sample titration, the last measured drift value is adopted automatically. This value is taken into account in the result calculation. Result = determined amount of water Ð (drift• titration time).
For accurate results, the **drift value** should therefore be **as stable and as low as possible** before the titration starts!

## 5.2 Titrant concentration

The titrant concentration can change for the following reasons (see also Section 2):

1. The titrant is not chemically stable, e.g. the one-component titrant.
2. The titrant may absorb moisture from the atmosphere reducing its concentration (the anhydrous methanol in the titrant is extremely hygroscopic)
   - if the desiccant on the titrant bottle is "used up" (see Section 5.1.2),
   - if the titrant bottle is not tightly sealed.
3. A significant change in temperature may occur:
   The Karl Fischer titrants consist of approximately 90% methanol or ethanol. Their volume increases considerably with temperature, so that there is a sharp drop in concentration (see Section 5.5).

### 5.2.1 How often should the concentration be determined?

How often the concentration is determined depends on the choice of titrant, the tightness of the titrant bottle and the desired level of accuracy.

Based on the chemical stability of the titrant, a weekly titer determination would be sufficient (the concentration of the one-component titrant changes by 0.01mg/mL per week, while the two-component titrant is stable).

**We recommend determining the titrant concentration daily.**

In countries where the temperature varies considerably during the course of the day and the lab is not air-conditioned, it is better to determine the concentration every 2 to 4 hours (see Section 5.5).

The tightness of the titration stand and the proper functioning of the burette and the end point indication are also checked at the same time as the concentration is determined. This test of the complete system is therefore an essential precondition for accurate, reproducible results.

**DL31/DL38**: These titrators allow you to define a time interval for the concentration determination of each titrant (see Section 5.2.4; DL31/DL38). When this time expires, the message "CONC determination due!" appears at the start of every determination. This is also documented on the GLP report as "Redetermine concentration!".

Notes

1. Either rinse the burette or dispense 2 to 3 mL of titrant into a waste bottle before you determine the concentration first thing in the morning. The plastic tubing of the burette is not absolutely water vapor-tight, so that the concentration of the titrant inside it decreases slightly when left to stand for a long time.
2. Determine the concentration under the same conditions as used for sample analysis. "Same conditions" means
   - using the same titration stand with the same volume of solvent,
   - at the same temperature (see Section 5.2, point 3).

### 5.2.2 Concentration determination with di-sodium tartrate · 2 $H_2O$

*General*

Di-sodium tartrate · 2 $H_2O$ is the primary standard for the Karl Fischer titration. Under normal conditions this substance has a water content of 15.66%; it is stable and non-hygroscopic. Since di-sodium tartrate only dissolves slowly in methanol, you should reduce it to a fine powder before using it (see Section 5.4.5).

*Procedure*

Ð Weigh between 0.04 and 0.08 g di-sodium tartrate with the aid of a weighing boat and add to the titration vessel: This weight yields an optimum titrant consumption of 1.3 to 2.5 mL with a 5 mL burette.

Ð Make sure when you add the di-sodium tartrate that none of it adheres to the beaker wall or to the electrode.

Ð Determine the weight by back weighing and enter it.

Ð Mix for 2 to 3 minutes (dissolve fully!) before you start the titration.

*Solubility of di-sodium tartrate*

The di-sodium tartrate must be completely dissolved (clear solution!) to obtain correct results. A cloudy solution will falsify the results (too high). You should therefore always take into account the restricted solubility of di-sodium tartrate in the solvents most commonly used for Karl Fischer titrations:

| | |
|---|---|
| In Solvent* | highly soluble, mixing time 1 minute. You can perform six determinations in 30 mL of Solvent* before you need to change it. |
| In Solvent*/chloroform mixture 1:1 or Solvent*/decanol mixture 1:1 | slightly soluble, mixing time 5 minutes. You can only perform one determination in 50 mL of 1:1 mixture (with 0.05g di-sodium tartrate). You must either change the solvent after every sample or use pure Solvent* for the determination. |
| In Solvent*/formamide mixture 1:1 | highly soluble, mixing time 1 minute. |
| In methanol | less soluble, mixing time 2 to 3 minutes. You cannot perform more than three determinations in 40 mL of methanol (with 0.045 g di-sodium tartrate). |
| In methanol/chloroform mixture 1:1 or methanol/decanol mixture 1:1 | partially soluble. The values obtained are approximately 10% too high. You must perform the determination in pure methanol! |
| In methanol/formamide mixture 1:1 | highly soluble, mixing time 1 minute. You can perform eight determinations in 40 mL of this mixture before you need to change the solvent. |
| In solvent for aldehydes and ketones (one-component reagent) | partially soluble. The values that are obtained are approximately 30% too high. You must perform the determination in pure methanol! |
| In ethanol | less soluble, mixing time 2 to 3 minutes. You cannot perform more than two determinations in 40 mL of ethanol (with 0.05 g di-sodium tartrate). |

* Solvent: solvent for the two-component reagent

### 5.2.3 Concentration determination with Water Standard 10.0

*General*

"HYDRANAL¨-Water Standard 10.0" from Riedel-de Ha‘n consists of a solvent mixture with a precisely determined water content (10.0 mg water/g). This content is confirmed by the test certificate enclosed with every pack. The water standards are supplied in glass ampoules. They are thus protected against the ingress of moisture and can be stored for up to five years.

*Procedure*

To achieve an optimum consumption of 2 to 3 mL titrant with a concentration of 5 mg/mL, you should weigh in 1.0 to 1.5 g of water standard 10.0 (see also Section 5.4.3).

Ð Open the ampoule shortly before the measurement in accordance with the enclosed instructions.

Ð Rinse a 10 mL syringe with approximately 1 mL of water standard.

Ð Draw the complete contents of the ampoule into the 10 mL syringe.

Ð Inject 1 to 1.5 mL at a time as an aliquot and determine the weight by back weighing. The contents of the ampoule is sufficient for 3 to 5 determinations.

Ð Start the titration without any mixing time.

Notes

1. The water standard is highly soluble in all the solvents commonly used for Karl Fischer titration and can therefore be used without restrictions.
2. You can use a water standard with 1.0 mg water/g for a titrant concentration of 2 or 1 mg/mL.
3. Use a new ampoule for each new concentration determination. With an open ampoule there is a risk of moisture ingress, which would falsify the results.
4. You reduce the influence of the atmospheric moisture by drawing the complete contents of the ampoule into the syringe.
5. Plastic syringes may introduce a small amount of moisture. You minimize this error by rinsing and conditioning the syringe beforehand. Glass syringes are better.

### 5.2.4 Concentration determination with water

*General*

Using pure water to determine the concentration requires a good deal of practice and precise working to obtain reproducible, accurate results, due to the very small amount of sample (10 to 20 µL). We therefore recommend determining the concentration either with di-sodium tartrate or with Water Standard 10.0.

*Procedure*

You must weigh in between 10 and 20 µL of deionized water or water according to ISO 3696 for a consumption of 2 to 4 mL titrant with a concentration of 5 mg/mL.

The sample should be weighed either using a balance with a resolution of 0.01 mg (e.g. METTLER TOLEDO AT261 balance) or with a 10 or 20 µL precision syringe (e.g. Hamilton microliter syringe, Type 810 RNE). A balance with a resolution of 0.1 mg does not satisfy the requirements for a reproducible titration.

Ð Inject exactly 10.0µL deionized water with a 10 µL syringe.

Ð Enter 0.01 g as the weight.

Ð Start the titration without any mixing time.

Notes

1. It is possible to determine the titrant concentration with water in all the solvents commonly used for Karl Fischer titration. For multiple determinations with consecutive titrations, you must take the solvent capacity into account (see Section 5.3.2).

2. You should always observe the following points when determining the concentration with a 10 µL syringe:

   Ð Precondition the 10 µL syringe for approximately one hour by filling it with water. All the screws in the syringe must be tightened securely.

   Ð You can get rid of any bubbles in the syringe by expelling the water rapidly.

   Ð Do not warm the syringe. Always use a syringe with a long metal shaft, to avoid touching the glass part.

   Ð Adjust the plunger to exactly 10.0µL; hold the syringe at right angles directly in front of your eyes to read off the value.

   Ð After setting the volume, wipe off any drops that have adhered to the needle with two fingers (be careful if you use a paper towel; if it is absorbent, it may draw water out of the needle!).

   Ð Always add the samples in exactly the same way.

   → If you are using a METTLER TOLEDO titrator, insert the syringe through the 1 mm hole of the three-hole adapter, lay it down on the adapter and empty it completely (see Section 5.4.4).

**DL31/DL38**: With these titrators you can start a "CONC" determination, select the stored water standard 10 and enter the water content stated on the test certificate.
At the end of the titration, the titrator calculates the concentration, e.g. 4.9876, and automatically stores this value as a parameter for the titrant used. The date and time of the determination are also entered.

Example for the one-component reagent with a concentration of 5 mg/mL

```
1-comp 5       SETUP
--------------------
Name        1-comp 5
Conc.[mg/mL]  4.9876
Type     1 component
Burette         5 mL
Fill rate [%]    100
Batch          72630
Check after [day]  0
Date      28-09-1998
Time           14:32
```

## 5.3 The solvent

To determine the water content in a sample, this sample must be dissolved. The water must be freely available, so that it can react with the Karl Fischer reagent. You can use various solvents for this purpose. Part of the solvent must always be an alcohol (preferably methanol), to ensure that the Karl Fischer reaction is stoichiometric (see Sections 1 and 1.3).

### 5.3.1 Common solvents and their applications

| Solvent | Maximum amount | Samples |
|---|---|---|
| Methanol | 100% | Solvents: toluene, dioxane, alcohols, ester<br>Organic products: urea, salicylic acid<br>Foods: honey, yogurt, beverages<br>Cosmetics: soaps, creams, emulsions |
| Chloroform | 70% | Petrochemical products: crude oil, hydraulic oil, transformer oil, fat |
| 1-Decanol<br>Hexanol<br>Dodecanol | 50% | Oils: edible oil, massage oil, ethereal oils<br>Petrochemical products: gasoline, diesel oil, kerosene<br>Pharmaceutical products: ointments, fatty creams |
| Toluene | 50% | Waxes, tar products, suppositories |
| Formamide | 50 (30)% | Sugar products: jelly, caramel, jelly bears<br>Starch products: flour, corn, noodles, potato chips |

Notes

1. The solvents that are used should contain as little water as possible (<100 ppm), or the titration will take too long and titrant will be wasted.
2. If you titrate acidic or basic samples, you must add buffering agents to the solvent to ensure that the titration is quick and without side reactions: use imidazole for acidic samples and salicylic or benzoic acid for basic samples (see Sections 1 and 1.3).
3. Sugar is the only type of sample that dissolves in formamide. Starch products will not dissolve; on the other hand, formamide extracts the water from them extremely effectively. You can optimize the extraction capacity by increasing the temperature (50 °C). The amount of formamide at 50 °C should not exceed 30%, or the stoichiometry of the Karl Fischer reaction will change and the results falsified.

### 5.3.2 Dissolving capacity of the solvent

The dissolving or extraction capacity of the solvent is an important factor in Karl Fischer titrations. If exhausted, the water will no longer be completely released giving incorrect results. You must therefore replace the solvent timely.

The solvent for the two-component reagent contains $SO_2$, which may be completely expended if you titrate a large number of samples with a high water content; the titration will then be very slow. Once again, you must replace the solvent timely.

**DL31/DL38**: These titrators can monitor the solvent capacity: you define when the solvent should be replaced by specifying the titrant consumption in milliliters. The titrator accumulates the titrant consumption continuously during titrations and reports "Solvent capacity exhausted" as soon as the specified value is exceeded.

## 5.4 The sample

### 5.4.1 Sampling

When taking samples for a water determination, you must work extremely carefully to exclude atmospheric moisture Ð the most common source of errors. If the water content of a sample changes during sampling as a result of moisture being absorbed or desorbed, you will no longer be able to determine its true water content.

**An analysis cannot be better than the actual sample!**

Observe the following points:

1. The sample must contain the average amount of water for the material being examined as a whole.
2. The sample should be taken quickly to exclude Ð or at least reduce to a minimum Ð the possibility of changes due to moisture being absorbed or evolved.
3. Heterogeneous water distribution in samples:
   - In non-polar liquids, such as oils, the water is coarsely dispersed, floats on the surface or settles on the bottom. You must mix liquids of this type thoroughly before taking a sample (by shaking them!).
   - In the case of non-polar solids, such as butter, which cannot be mixed as thoroughly as liquids, the sample should be larger the more heterogeneous the distribution of the water.
4. Substances with a very high water content:
   - If a solid has a high water content, but evolves water easily, the content is usually lower on the surface than inside.
5. Hygroscopic substances:
   - Hygroscopic solids may have a higher water content on the surface than inside if they have absorbed atmospheric moisture during storage.
6. Substances with a very low water content:
   - Substances with a very low water content are often also extremely hygroscopic. The sample must therefore be taken very quickly and with a syringe or a spatula that is absolutely dry (see Section 5.4.4).

### 5.4.2 Storing the sample

After you have taken the sample, you should determine the water content as soon as possible. If you must store the sample, keep it in a tightly sealed bottle.

Ð Glass bottles are preferable to plastic bottles, because plastic is not absolutely water vapor-tight. If the sample has to be stored for a very long time, you can keep it in a sealed glass ampoule.

Ð Use sample bottles with openings as small as possible, to keep the ingress of moisture to a minimum. You can use bottles with a septum stopper for liquids with a very low water content.

Ð Use glass bottles with a gas-tight screw cap; tapered caps are unsuitable.

Ð Choose a bottle size equivalent to the amount of sample: the smaller the gas space above the sample, the smaller will be the amount of moisture.

Ð Clean the glass bottles by rinsing them with methanol and dry them in the drying oven. You can assemble bottles with a septum stopper when hot.

Ð Rinse the bottles two or three times beforehand with the sample, if the sample is a liquid.

Ð Store the sample bottles under normal conditions: with solids, adherent moisture may diffuse to the part of the bottle that is colder (e.g. if the bottle is left standing by a cold window).

If the water in a liquid sample has not dissolved, it may be separated out if the sample is left to stand for a long time. This can also happen if the solubility limit for water is exceeded when the sample cools down. In this case you can stabilize the solution with a solubility promoter, e.g. 2-propanol.

### 5.4.3 Amount of sample

The amount of sample depends on the expected water content and the desired degree of accuracy (see also Section 6). If a high level of accuracy is required, the amount of sample should be such that the titrant consumption is between 30 and 70% of the burette volume. This corresponds to 7.5 to 17.5 mg water per sample for a 5 mL burette and a titrant concentration of 5 mg/mL.

The optimum amount of water is 10 mg per sample.

As a rule of thumb, the accuracy increases with the amount of sample, because the absorption of atmospheric moisture during sampling and sample addition has less effect.

*Determination of the amount of sample for water contents less than 1000 ppm*

Determinations of water traces are not required to be quite as accurate: a relative standard deviation of 1 to 5%, determined with repeatability, is considered acceptable. A titrant consumption of 0.1 to 0.05 mL is thus still acceptable for a 5 mL burette. This corresponds to 0.1 to 0.05 mg water per sample with a titrant concentration of 1 mg/mL.

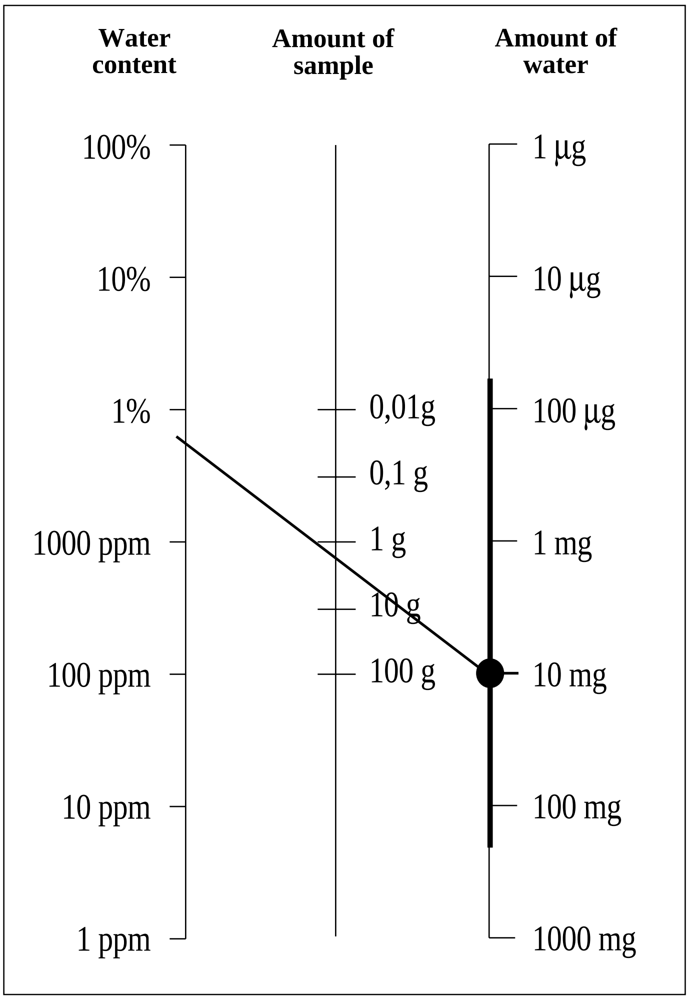
If you need to determine water traces more accurately (10 ppm to 1000 ppm), you should use a titrant with a lower concentration (1 or 2 mg/mL) and adhere to the following minimum sample weights:

| | | | | | | |
|---|---|---|---|---|---|---|
| Water content [ppm]: | 1000 | 500 | 200 | 100 | 50 | 10 |
| Minimum weight [g]: | 2 | 3 | 4 | 5 | 7 | 8 |

Example: Titration of "dry" toluene with the DL38 titrator

| | |
|---|---|
| 6 samples: mean value = 12.2 ppm, standard deviation = 0.7 ppm, rel. standard deviation = 5.8 % | |
| Sample weight: | 8 g (corresponds to 0.1 mg water per sample) |
| Titrant consumption: | 0.06 mL (titrant concentration: 2 mg/mL) |

*Determination of the amount of sample for water contents of 1000 ppm to 100%*

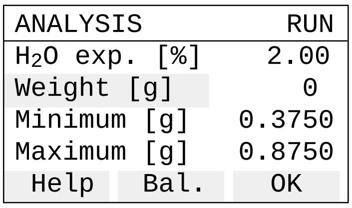


Starting from the optimum point (10 mg) or the recommended range, the best possible amount of sample can be determined as a function of the expected water content. For this, the optimum point is connected by a straight line to the expected water content. The intersection point of this line with the "Amount of sample" scale represents the best possible amount of sample.

**Notice**: Logarithmic scale!

Example:
Expected water content: 5000 ppm
Optimum amount of water: 10 mg/sample
Optimum amount of sample: 2 g

**DL31/DL38**: These titrators allow you to enter the expected water content when the amount of sample is requested. The titrator immediately calculates minimum and maximum values for a titrant consumption of 30 to 70% of the burette volume.

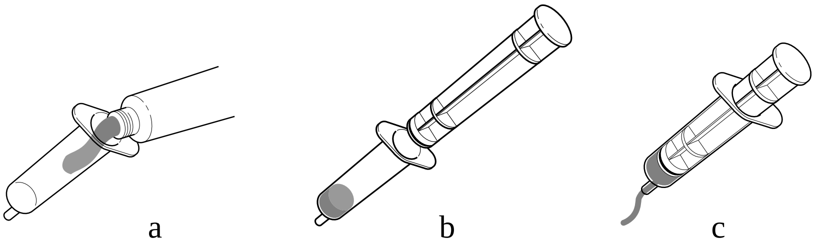


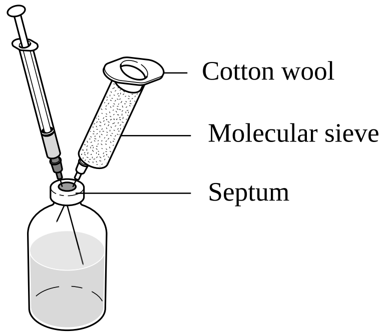
```
ANALYSIS            RUN
H2O exp. [%]       2.00
Weight [g]            0
Minimum [g]      0.3750
Maximum [g]      0.8750
 Help    Bal.      OK
```

### 5.4.4 Addition of liquid samples

If you add liquid samples, you must take appropriate steps to prevent atmospheric moisture from being absorbed, particularly if these samples have a low water content. The following methods are suitable for the various types of liquid sample.

*Addition techniques*

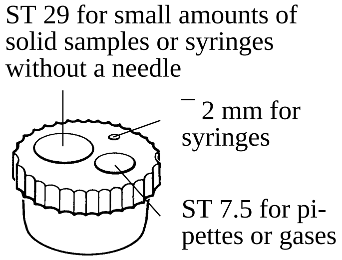
| **Sample characteristic** | **Procedure** |
|---|---|
| High water content,<br>low viscosity | e.g. beverages, perfume, watery emulsions:<br>Ð Inject the sample into the titration vessel either through a septum or through the needle hole in the three-hole adapter using a 1 mL **syringe with needle** (see diagram overleaf). |
| Low water content,<br>hygroscopic,<br>low viscosity<br><br>Thick, viscous | e.g. methanol, hexane, toluene, gasoline, edible oil:<br>Ð Store the sample in a bottle with a septum stopper (see diagram overleaf).<br>Ð Rinse a 10 mL syringe two or three times with the sample.<br>Ð Inject the sample into the titration vessel either through a septum or through the needle hole in the three-hole adapter using a **syringe with needle**. |
| Extremely viscous | e.g. glycerol, hydraulic oil, silicone oil, massage oil:<br>Ð Inject the sample into the titration vessel through the small hole in the three-hole adapter using a 5 or 10 mL **syringe without needle**. |
| | e.g. honey, yogurt, ointments, creams:<br>Ð Fill the sample into a 5 or 10 mL syringe from behind, e.g. the cream in a tube (a).<br>Ð Insert the plunger into the syringe (b).<br>Ð Add the sample to the titration vessel through the large hole in the three-hole adapter using a **syringe without needle** (c).<br> <br>You can use a syringe without a base or with the base drilled out for highly viscous pastes. |
| Waxy | e.g. candles, paraffin, ski wax, suppositories:<br>Ð Liquefy the samples in a drying oven at approx. 50 °C and fill them into a syringe. The syringe is heated up together with the wax. This prevents the sample from hardening inside the syringe during the weighing process. |



*Taking samples from a bottle with a septum stopper*

After several samples have been taken, a vacuum will develop inside the bottle, so that it will no longer be possible to take a sample. In this case you must aerate the bottle with dry air:

Ð Fill a syringe without a plunger with molecular sieve, seal it with cotton wool and insert it into the septum with a short needle. Air will then be replenished via the molecular sieve when you take the next sample.



*Three-hole adapter for METTLER TOLEDO KF titration vessels*

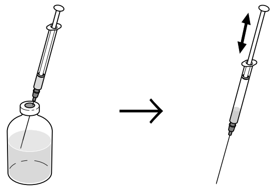
The three-hole adapter has a number of advantages over a silicone septum when syringes are used:

Ð It is always better sealed than the silicone septum: there is less drift in the titration stand.

Ð It is resistant to solvents such as chloroform and toluene (material: polypropylene), whereas the silicone septum is not.

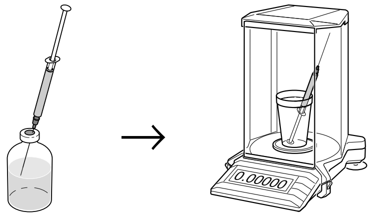
Ð If the syringe has a long, thin needle, e.g. Hamilton µL syringes, there is always a risk that the needle will be bent or broken off when the septum is pierced. This problem is avoided if the sample is added through the 2 mm hole in the three-hole adapter, because you can lay the syringe down on the stopper to empty it.

*Weight of liquid samples with the back weighing technique*



Ð Fill a quarter of the syringe with sample. Use bottles with a septum stopper and pressure compensation if the sample is hygroscopic or has a low water content (<1000 ppm) (see diagram above).

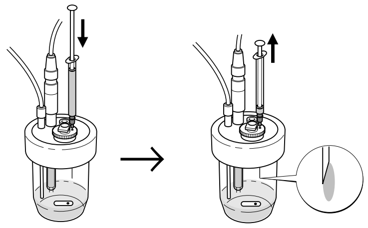
Ð Pull up the plunger and rinse the syringe with the sample by shaking it.



Ð Empty the syringe (waste bottle) and rinse again two or three times.

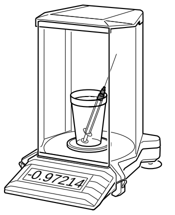
Ð Fill the syringe with sample and wipe the needle with a paper towel.

Ð Place the syringe with the sample in a beaker on the balance (upside down!) and tare the balance.



Ð Inject the sample into the titration vessel.

Ð Retract the plunger so that the drop at the needle tip flows back into the needle. Otherwise, when the syringe is removed, the drop will adhere to the adapter.



Ð Return the syringe with the rest of the sample to the beaker on the balance again and weigh it back.

Ð Enter the weight on the titrator or transfer automatically.

Ð **Start the titration!**

**Metering liquid samples**

You can use bulb pipettes for large volumes (5 to 25 mL) and glass syringes with a calibrated cylinder for small volumes (<5 mL). You should always rinse the bulb pipettes or glass syringes two or three times beforehand with the sample.

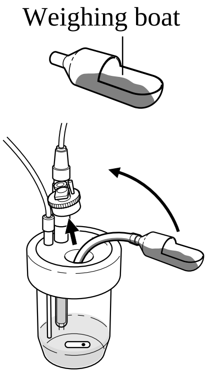
Notes

1. How to use glass syringes with very small volumes (10 to 100 µL) is described in Section 5.2.4, Note 2.
2. You can normally improve the accuracy by weighing the sample!

### 5.4.5 Addition of solid samples

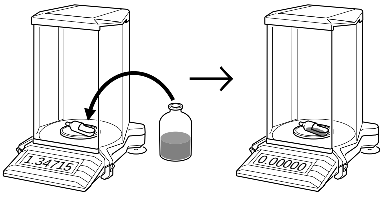
You can add solids to the titration vessel directly. The sample should be weighed and added quickly to minimize atmospheric exposure and under normal conditions, i.e. just as it was transported and stored. The storage of samples in a refrigerator may cause water to condense; warm such samples to room temperature in a closed vessel before you weigh them.

*Addition techniques*

| Sample characteristic | Procedure |
|---|---|
| Brittle, hard/soft, pourable | e.g. salts, crystalline samples:<br>Ð Grind hard, coarse-grained samples in a closed, cooled analytical mill; pulverize less hard samples in a mortar.<br>Ð Add the sample with a weighing boat.  |
| Finely powdered, dusty | Ð Use a weighing boat with flexible tubing to add the sample: this will prevent the sample from adhering to the wall of the titration vessel or to the electrode. |
| Finely powdered with very low water content | e.g. salicylic acid, cellulose powder:<br>Ð Either weigh the sample in a dry box or extract it externally (see Section 7.2). |
| Viscous | e.g. jellied fruits, jelly bears, marzipan:<br>Ð Cut into small pieces with scissors or a knife and add the sample with a spatula. |
| Hard, fatty | e.g. chocolate, solid fat:<br>Ð Grate the product and add the sample with a spatula. |

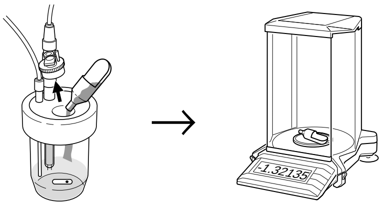
| Sample characteristic | Procedure |
|---|---|
| Soft, fatty, inhomogeneous | e.g. butter, margarine, edible fat:<br>Ð Homogenize the sample well: the water is distributed inhomogeneously since it is not dissolved in the sample. The water content is often lower on the surface than in the middle of the sample.<br>Ð Add the sample with a spatula. Do not use a syringe, because the water is forced out if it is pressurized. |
| Waxy | e.g. candles, paraffin, ski wax, suppositories:<br>Ð Liquefy the samples in a drying oven at approx. 50 °C and fill them into a syringe. The syringe is heated up together with the wax. This prevents the sample from hardening inside the syringe during the weighing process. |

*Weight of solid samples with the back weighing technique*



Ð Weigh the sample in the weighing boat and tare the balance to zero.

Ð Add the sample to the titration vessel. Use a weighing boat with flexible tubing if necessary, to prevent the sample from adhering to the vessel wall or to the electrode.



Ð Back weigh the empty weighing boat.

Ð Enter the weight on the titrator or transfer automatically.

Ð **Start the titration!**

## 5.5 Effects of temperature

*On the titrant*

The Karl Fischer titrants consist of approximately 90% methanol or ethanol. Their volume increases considerably if the temperature rises, and their concentration decreases accordingly. S. Eberius [7] specifies a correction factor of 0.0012 per degree Celsius for methanolic Karl Fischer solutions. According to ISO 760, a temperature rise of 1 °C causes a drop of 0.1% in the concentration.

The titrant (especially that for the two-component reagent) may outgas if the temperature rises. This causes bubbles to form in the titrant tubing, an effect which is worse the faster the rate at which the burette is filled.

**DL31/DL38**: These titrators allow you to define the filling rate of the burette separately for each titrant, e.g.:

| Temperature [°C]: | < 15 | 15 Ð 30 | > 30 |
|---|---|---|---|
| Filling rate for one-component titrant [%] | 100 | 100 | 70 |
| Filling rate for two-component titrant [%] | 80 | 60 | 40 |

*Titration at low temperatures*

You can perform Karl Fischer titrations at low temperature to eliminate unwanted side reactions. The water content of peroxides, for example, can be determined at -40 °C. You must use the two-component reagent to do so, because the reaction rate of the one-component reagent is too slow at this temperature.

*Titration at high temperatures*

Increasing the titration temperature speeds up the dissolution of the sample or the extraction of the water from it, resulting in shorter titration times (see Section 7.1). Titrations at elevated temperature have proved particularly effective for foodstuffs, e.g. sugar, flour, potato flakes, hazelnuts, custard powder.

The maximum temperature depends on the boiling point of the reagent (boiling point of methanol: 64 °C, boiling point of ethanol: 78 °C).

## 5.6 Side reactions

Side reactions that falsify the results can occur parallel to the Karl Fischer titration.

1. *Reaction with methanol*

   Aldehydes and ketones react with methanol to form acetals and ketals as well as water:

   Formation of acetal: $CH_3CHO + 2\,CH_3OH \longrightarrow CH_3CH(OCH_3)_2 + \mathbf{H_2O}$

   Formation of ketal: $(CH_3)_2CO + 2\,CH_3OH \longrightarrow (CH_3)_2C(OCH_3)_2 + \mathbf{H_2O}$

   **Measures**: Use the special reagents for aldehydes and ketones with these substances (see Section 2.4).

   Experiments have shown that the side reaction still takes place despite these reagents. Each time acetone is determined, for example, the drift is higher than before the titration: the larger the sample, the greater the drift increase. We therefore recommend performing the determination with a small sample amount and replacing the solvent after two or three samples.

2. *Reaction with water*

   Another side reaction Ð bisulfite addition Ð occurs with aldehydes in the presence of $SO_2$. Water is consumed in the process:

   Bisulfite addition: $CH_3CHO + \mathbf{H_2O} + SO_2 + NR \longrightarrow HC(OH)SO_3HNR$

   **Measures**: Start the titration immediately after adding the sample. This causes the water to be titrated quickly, before any bisulfite addition can take place.

   **DL38**: This titrator has an "Auto start" parameter: the titrator starts titrating automatically as soon as the sample has been added and water is detected.

3. *Reaction with iodine*

   The Karl Fischer reaction is a REDOX reaction with iodine as the oxidizing agent. Iodine may thus also react with readily oxidizable samples; in the presence of certain samples, e.g. oxides, it can also be reduced by $SO_2$. Both reations cause additional iodine being consumed, giving a false higher water content. The following substances can react with iodine:

Ascorbic acid
Boric acid
Disulfite $S_2O_5^{2Ð}$
Hydroxide $HO^{Ð}$
Mercaptans RSH
Peroxide ROOR
Sulfite $SO_3^{2Ð}$
Tin(II) salts
Arsenite $AsO_2^{Ð}$
Tetraborate $B_4O_7^{2Ð}$
Iron(III) salts
Hydrogen carbonate $HCO_3^{Ð}$
Nitrite $NO_2^{Ð}$
Selenite $SeO_3^{2Ð}$
Tellurite $TeO_3^{2Ð}$
Arsenate $AsO_4^{3Ð}$
Carbonate $CO_3^{2Ð}$
Hydrazine + derivatives
Copper(I) salts
Oxides CaO, MgO, $MnO_2$
Silanol $R_3SiOH$
Thiosulfate $S_2O_3^{2Ð}$

**Measures**: You can perform the Karl Fischer titration for the majority of these substances with the aid of the drying oven (see Section 7.5).

### DL31/DL38: Reevaluation following side reactions

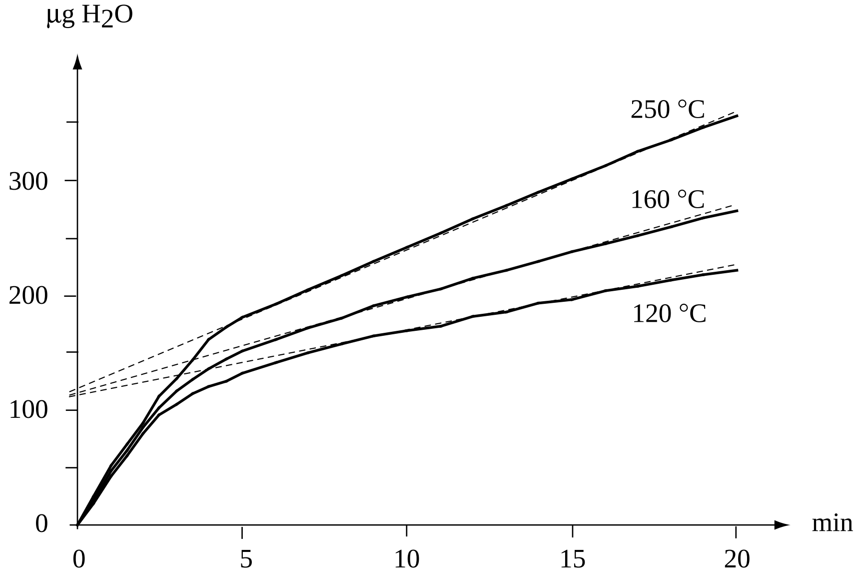
The water content calculated for the sample is too high if side reactions described under points 1 and 3 have occurred. This can also be the case if a drying oven is used for the determination and the sample decomposes slowly. You can determine the correct result with a reevaluation of the volume/time curve.

Example: Water determination for red polypropylene fibers

The determination was carried out for a period of 20 minutes with the drying oven set to 120 °C, 160 °C and 250 °C. The following results were obtained:

¥ 1186 ppm at 120 °C
¥ 1442 ppm at 160 °C
¥ 1955 ppm at 250 °C.

The volume/time curve clearly indicates the occurrence of a side reaction, which is faster the higher the temperature. The "water content" rises along with the temperature. You can use the DLWin software to export the measured values to EXCEL and reevaluate them.



The actual water content of the sample can be obtained by extrapolating the titration curve to time zero. The content in the example shown here is 115 mg water; this corresponds to a water content of 640 ppm for a sample weight of 0.18 g. The sample was also extracted externally in methanol to perform a comparative determination. The result obtained with this method was 610 ppm.

# 6 Measurement results

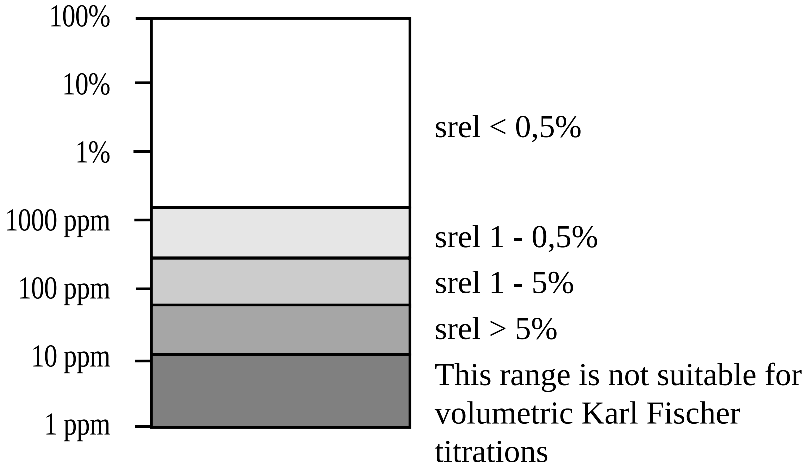
## 6.1 Measurement accuracy

With Karl Fischer titrations you can determine the closeness of agreement between the result of measurement and the true sample value either by conducting reference measurements or by titrating samples with a known water content. The measurement accuracy depends on all the various factors described and explained in the previous sections. The crucial factors are optimum control as well as the water content and the amount of the sample.

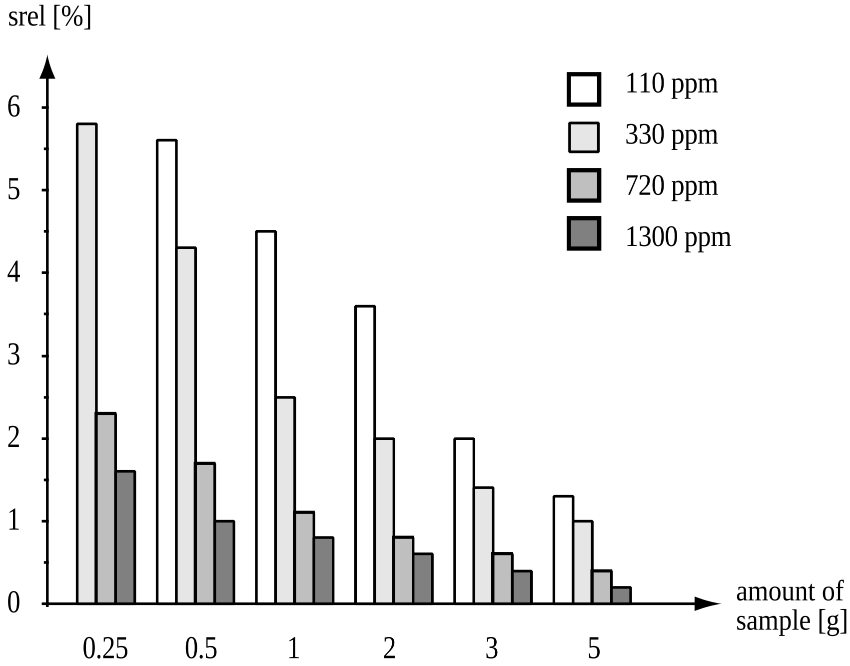
## 6.2 Repeatability

The closeness of the agreement between the results of successive measurements of the same sample can be expressed quantitatively as the relative standard deviation (srel). Assuming optimum control and the best possible amount of sample, the following values can be obtained for this parameter under repeatability conditions:

*Relative standard deviation for different water contents*



*Amount of sample versus srel for different water contents*



# 7 Special Karl Fischer methods

Karl Fischer titration is only possible if the water in the samples is freely available. This is not the case with solids if the water is bound, e.g.

- in cells (plants),
- in capillaries (minerals),
- as waters of crystallization (salts).

Special sample preparations and special Karl Fischer methods are necessary to free the water in these samples.

*Sample preparation*

You must crush insoluble solids in order to gain access to the trapped water. The following methods are available:

| **Sample characteristic** | **Procedure** |
|---|---|
| Very hard | e.g. minerals, hard salts:<br>Grind in a closed, cooled analytical mill. |
| Hard, brittle | e.g. inorganic salts, grain, noodles, coffee beans:<br>Crush in a mixer. |
| Moderately hard, brittle | e.g. organic salts, crystalline products:<br>Pulverize in a mortar. |
| Viscous | e.g. jellied fruits, jelly bears, marzipan:<br>Cut into small pieces with scissors or a knife. |
| Hard, fatty | e.g. chocolate, solid fat:<br>Grate the product. |
| Soft, fatty | e.g. sausage, meat, cheese:<br>Mince the product, then reduce it further with a homogenizer in an external solvent. |
| Fibrous natural products | e.g. dried fruit and vegetables, berries:<br>Reduce with a homogenizer in an external solvent. |
| Suspensions | e.g. fruit juice extracts, vegetable juices:<br>Reduce with a homogenizer. |

## 7.1 Internal extraction

Internal extraction is suitable for insoluble solids that evolve water quickly when crushed.

Ð Add the crushed samples to the titration vessel, using either methanol or a mixture of formamide and methanol as the solvent; the water is then extracted providing the mixing time is sufficiently long. You can speed up the extraction of the water by

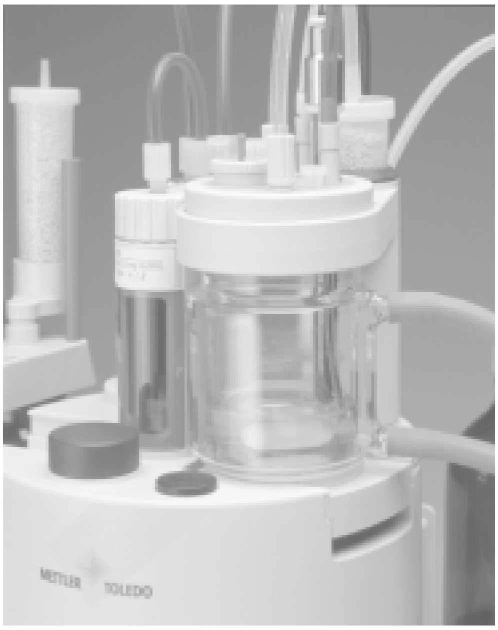
¥ heating the solution with a thermostatable titration beaker,
¥ reducing the sample further with a built-in homogenizer (see photos below).

Examples (see also METTLER method No. 904):

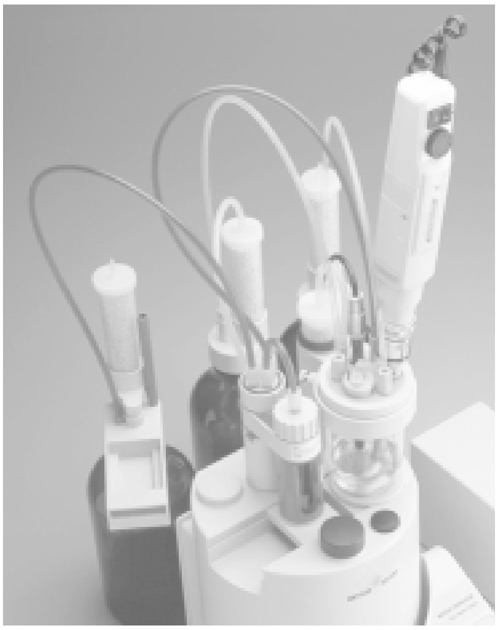
| **Sample** | **Result** | **srel** | **Solvent** |
|---|---|---|---|
| Flour | 12.1 % | 0.4 % | Formamide / methanol 2:3 at 50 °C |
| Potato chips | 4.8 % | 0.8 % | Formamide / methanol 2:3 at 50 °C |
| Ground hazelnuts | 4.8 % | 1.2 % | Formamide / methanol 2:3 at 50 °C |
| Chocolate | 1.3 % | 1.1 % | Methanol / homogenizer |
| Instant coffee | 2.5 % | 1.4 % | Methanol / homogenizer |
| Dried chives | 8.0 % | 1.0 % | Methanol / homogenizer |
| Dried tarragon | 7.3 % | 1.4 % | Methanol / homogenizer |
| Aspirin | 1.5 % | 1.9 % | Methanol / homogenizer |
| Sweetener tablets | 1.1 mg/pc | 0.9 % | Methanol / homogenizer |
| Optical bleaching agent | 3.9 % | 0.8 % | Methanol |

Note
In many cases, the homogenizer eliminates the need for formamide with, e.g. hazelnuts, potato chips, etc.

DL38 with thermostatable beaker



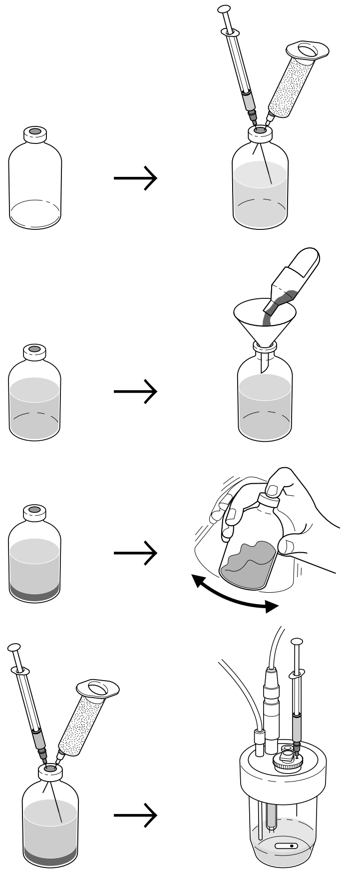
DL38 with built-in homogenizer operating at approx. 20 000 rpm.



## 7.2 External extraction

External extraction is suitable for insoluble solids that only evolve water slowly when crushed, as well as for samples with an extremely inhomogeneous water distribution.

Ð Add the finely crushed sample to a solvent with a very low water content and leave it to stand until the water has been extracted. You can speed up the extraction by
  ¥ shaking the solution (mechanical shaker, shaking bath),
  ¥ placing the solution in an ultrasound bath for a certain time,
  ¥ reducing the sample further with a built-in homogenizer.



*External extraction procedure*

Ð Weigh a bottle with a septum that is suitable to the amount of sample and solvent and note the weight.

Ð Pour the solvent into the septum bottle.

Ð Determine the water content of this solvent, i.e., determine the blank value (three determinations), and note the mean value as **f1**.

Ð Weigh the bottle again in order to determine the weight of the remaining solvent.

Ð Note this value as**f2** and tare the balance to zero.

Ð Add the sample to the solvent in the septum bottle.

Ð Weigh the bottle again in order to determine the weight of the sample.

Ð Note this value as**f3**.

Ð Perform the extraction (shake, mix, ultrasonic bath).

Ð Allow the sample to settle.

Ð Determine the water content of the supernatant solvent (three determinations).

The water content of the extracted sample is calculated using the following formula:

$$H_2O\text{ content} = x \cdot \left(\frac{f2}{f3} + z\right) - \frac{f1 \cdot f2}{f3}$$

x: Water content of the supernatant solvent in % or ppm
f1: Blank value of the solvent in % or ppm
f2: Amount of solvent after determining the blank value in g
f3: Amount of extracted sample in g
z: $\frac{x}{100}$ for % content and $\frac{x}{10^6}$ for ppm content

(The extracted water causes the mass of the solvent to increase; **z** takes account of this portion according to the titrated sample.)

**DL38**: The formulae for calculating the water content are stored in this titrator. You can apply them as follows:

Ð Select either "x [%] ext.extr." or "x [ppm]ext.extr" as the result for "Calculation 1" and enter the blank value of the solvent (f1) as the factor. (**Notice**: You must enter the blank value in the selected unit),

Ð select "No calculation" as the result for "Calculation 2" and enter the amount of solvent (f2) as the factor,

Ð select "No calculation" as the result for "Calculation 3" and enter the amount of extracted sample (f3) as the factor.

Notes

1. The water content of the solvent should be as low as possible, in order to maximize the extraction effect and ensure that the difference between the water contents before and after extraction is as large as possible.
2. The amount of sample should be sufficiently large to ensure that the amount of water in the sample is significantly greater than that in the solvent prior to extraction.
3. The amount of sample should also take account of the absorption capacity of the solvent. Chloroform, for example, reaches the saturation limit for water at 350 ppm!

Examples (see also METTLER method No. 905):

| **Sample** | **Result** | **srel** | **Solvent** |
|---|---|---|---|
| Cheese | 27.6 % | 0.4 % | Decanol / formamide / methanol 8:2:1 |
| Liver sausage | 61.6 % | 0.4 % | Decanol / formamide / methanol 8:2:1 |
| Mustard | 72.4 % | 0.6 % | Decanol / formamide 1:1 |
| Chicken broth | 4.9 % | 0.3 % | Decanol / formamide / methanol 8:2:1 |
| Tobacco | 11.5 % | 0.5 % | Methanol |
| Wool | 9.8 % | 0.4 % | Methanol |
| Acrylic paint | 54.3 % | 0.5 % | Formamide |

## 7.3 External dissolution

External dissolution is suitable for soluble solids with an extremely inhomogeneous water distribution or with a very low water content.

You must use a large amount of sample for substances with an inhomogeneous water distribution, in order to obtain a representative result. Direct titration is unsuitable, because with a large amount of sample it takes too long and uses too much titrant.

If the solid has a low water content (<200 ppm), the error that is produced with direct titration when the titration stand is opened to add the sample is too great. If 1 g of sample has a water content of 100 ppm (= 100 µg) for instance, the error as a result of opening the titration stand will be between 10 and 30 µg. Since you are able to work with larger amounts of sample if you choose external dissolution, the error is reduced.

This method is similar to external extraction, except that the sample is completely dissolved in the external solution. See also notes in Section 7.2.

The water content of the dissolved sample is calculated using the following formula:

$$H_2O \text{ content} = x \cdot \left(\frac{f2 + f3}{f3}\right) - \frac{f1 \cdot f2}{f3}$$

x: Water content of the external solution in % or ppm
f1: Blank value of the solvent in % or ppm
f2: Amount of solvent after determining the blank value in g
f3: Amount of dissolved sample in g

**DL38**: The formulae for calculating the water content are stored in this titrator. You can apply them as follows:

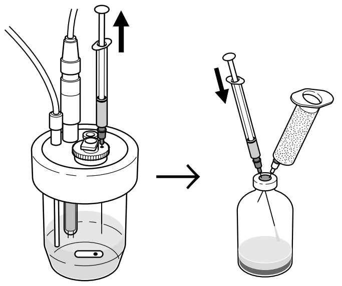
Ð Select either "x [%] ext.soln." or "x [ppm]ext.soln" as the result for "Calculation 1" and enter the blank value of the solvent (f1) as the factor. (**Notice**: You must enter the blank value in the selected unit),

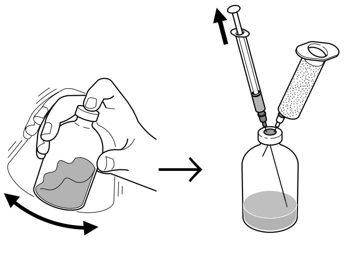
Ð select "No calculation" as the result for "Calculation 2" and enter the amount of solvent (f2) as the factor,

Ð select "No calculation" as the result for "Calculation 3" and enter the amount of dissolved sample (f3) as the factor.

## 7.4 Lyophilized substances in septum bottles

The extremely low water content of freeze-dried substances (e.g. biological tissue, serums, foodstuffs) in septum bottles means that external dissolution is inadvisable, because the blank value correction is too high in relation to the amount of water in the sample. You can proceed as follows:





Ð Remove approximately 10 mL titrated solvent from the titration vessel using a 20 mL plastic syringe with a long needle, and then return it to the vessel again.

Ð Rinse the syringe two or three times in this way until there is no water left inside it.

Ð Draw 10 mL of titrated solution into the syringe, weigh it and inject it into the septum bottle. Determine the weight by back weighing (see Section 5.4.4).

Ð Either shake the bottle or place it in an ultrasound bath for approx. five minutes to allow the lyophilized substance to dissolve or a suspension to form (in the latter case the sample must settle first before you can proceed to the next step).

Ð Draw the entire solution or an aliquot into the same syringe again, weigh it and inject it into the titration vessel. Determine the weight by back weighing.

¥ If the sample was completely dissolved, you can use the calculation formula for external dissolution (see Section 7.3);

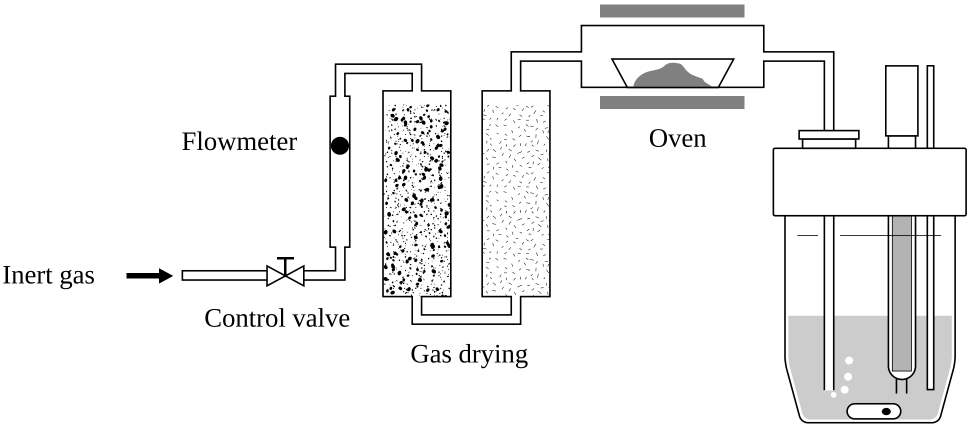
¥ If the sample was a suspension, you can use the calculation formula for external extraction (see Section 7.2).

**Notice**: Enter **0** for f1 under "Calculation 1" with both methods, as there is no blank!

## 7.5 Determination with the aid of a drying oven

This method is suitable for insoluble solids that form a side reaction with the Karl Fischer reagent or that only release water very slowly.

The sample is inserted into a glass tube in a metal or glass boat and heated. This causes the water in the sample to be released. The evaporated water is then transferred to the titration vessel with a dry, inert gas stream and the amount of water determined.



*Purge gas/ gas amount*

1. **Air** contains oxygen, which may react with the sample at high temperatures. You should therefore only use air for non-oxidizable, inorganic samples; if you use it for organic samples, the oven temperature should not exceed 160 °C.
2. If you take **nitrogen** from a cylinder, you should reduce the gas pressure in two stages so that the final pressure is around 0.5 bar. A gas stream of 150 to 200 mL/min is ideal. Experiments with various gas flow rates have yielded the following results:

| | | | |
|---|---|---|---|
| Gas flow rate [mL/min]: | 108 | 166 | 500 |
| Recovery [%]: | 99,9 | 99,7 | 97,1 |

*Purge gas drying*

The purge gases that are used normally contain moisture, e.g.

¥ Nitrogen from a high-pressure cylinder: between 1.4 and 8.0 mg/L,

¥ Air at 50 % atmospheric moisture: approx. 11 mg/L.

The residual moisture in the purge gas should be less than 50 µg/L for the Karl Fischer titration. You can use the following agents to dry the gas:

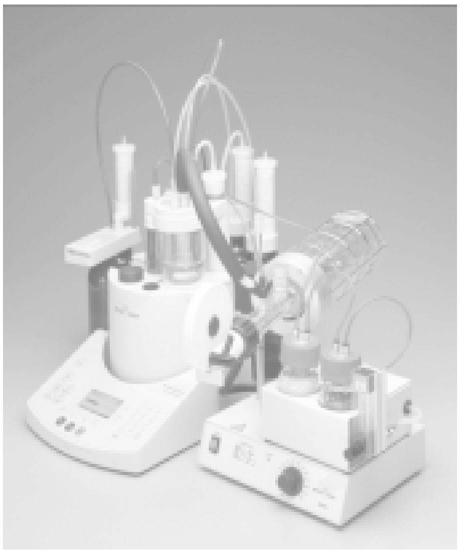
| **Agent** | **Residual moisture** | **Residual moisture stream for 200 mL/min** |
|---|---|---|
| Sulfuric acid 98% | 50 Ð 80µg $H_2O$/L | 10 Ð 15µg $H_2O$/min |
| Phosphorous pentaoxide | 40 Ð 50µg $H_2O$/L | 8 Ð 10µg $H_2O$/min |
| KF one-component titrant | 15 Ð 20µg $H_2O$/L | 3 Ð 4µg $H_2O$/min |
| Silica gel | 50 Ð 60µg $H_2O$/L | 10 Ð 12µg $H_2O$/min |
| Molecular sieve 3 • | 5 Ð 10 µg $H_2O$/L | 1 Ð 2µg $H_2O$/min |

Molecular sieve is the best desiccant in terms of residual moisture, but its water absorption capacity is relatively low. Silica gel is far superior in this respect. We therefore recommend drying the gas with a combination of silica gel and molecular sieve: start off with silica gel to absorb the majority of the water, then use molecular sieve to reduce the residual moisture to a minimum (see diagram). Silica gel and molecular sieve have the advantage that they can be regenerated, unlike other desiccants Ð silica gel at 150 °C and molecular sieve at up to 300 °C.

*METTLER TOLEDO drying ovens*

Our product range includes two drying ovens Ð the DO337 and the DO305. You can use both ovens with the DL31/DL38 titrators; their temperature range is 30 to 300 °C. Please refer to the relevant Operating Instructions for details of how to determine the water content.

DO305 drying oven with the DL38



The DO305 has a very large sample boat capable of holding up to 30 $cm^3$ of sample. This is particularly important for extremely lightweight samples, such as fibers, or for samples that have a very low water content.

Examples (see also METTLER method No. 906):

| **Sample** | **Result** | **srel** | **Temperature** | **Duration** |
|---|---|---|---|---|
| Polyamide | 5547 ppm | 0.8 % | 190 °C | 15 min |
| Polyethylene | 68 ppm | 6.9 % | 280 °C | 10 min |
| Engine oil | 842 ppm | 9.9 % | 140 °C | 15 min |
| Noodles | 10.1 % | 1.3 % | 140 °C | 15 min |
| Tobacco | 10.5 % | 2.4 % | 140 °C | 10 min |
| Paper | 5.0 % | 0.5 % | 140 °C | 15 min |
| Cement | 8200 ppm | 2.2 % | 300 °C | 20 min |

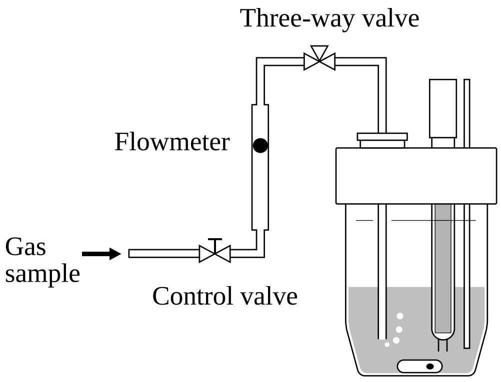
Notes regarding the DL31/DL38 titrator/drying oven system

1. Always start the titration before you place the sample in the oven to ensure that the correct drift value is adopted.
2. Select "Max. time" and a very low "Rel. drift stop", e.g. 1 µg/min, as termination parameters.

3. With some samples it takes a little time before the water starts evaporating. You should define a short mixing time (15 to 60 s) in this case, to prevent the titration from being terminated prematurely. You should avoid selecting the "Auto start" parameter for the same reason.
4. If you do not start the titration until all the water has been expelled from the sample, the water will not be completely titrated. Particularly if there is a large amount of water, it cannot be fully absorbed by the solvent. Experiments using methanol as the solvent produced a recovery rate of 98% for a gas stream of 166 mL/min; if the water is titrated as soon as it begins to evaporate, the recovery increases to 99.7%.
5. If you perform several water determinations in the same solvent, you should replace the evaporated methanol that has been lost in the gas stream depending on titration time and number of determinations. The methanol loss is 3.5 to 4 mL/h for an oven temperature of 200 °C and a flow rate of 200 mL/min. You can reduce the evaporation by adding between 20 and 30% ethylene glycol.
6. If you wish to validate the titrator/drying oven system, you can use the "HYDRANAL¨-Water Standard KF Oven" (Riedel-de Ha‘n). It consists of potassium citrate $\cdot H_2O$ and has a water content of 5.55%. It can be heated to 220 °C. This test also serves to check the tightness of the oven and the connection tubing!

## 7.6 Determination of water in gases

To determine the water content of gases, the gas must be directed through the titration vessel for a defined period of time.



The flow rate of the gas (200mL/min) should be as constant as possible to calculate the volume (necessary to calculate the water content).

**DL31/DL38**: These titrators calculate the water content in ppm by entering the volume and the density (see also METTLER method No. 907).

*Sampling/sample addition*

If possible, you should titrate the gas sample directly from the source. If not, you must fill the gas either into special gas sample tubes or into small steel cylinders.

Ð You must purge the sample vessels and the tubing thoroughly beforehand with the gas.

Ð If you use sample vessels, you can determine the amount of dispensed gas by differential weighing.

Ð If you are able to liquefy the gas, you should also inject it into the titration vessel in liquid form.

*Determination*

Ð Adjust the gas stream to a constant flow rate with the control valve: 50 to 200 mL/min, depending on the water content of the gas.

Ð Purge the system with the gas before you start the determination.

Ð Turn the three-way valve, to prevent the gas from flowing into the titration vessel.

Ð As soon as the drift is stable again, start the titration and reset the three-way valve to its original position in order to direct the gas into the titration vessel.

Ð Stop the gas flow after 1 to 2 mL titrant has been consumed.

Ð Calculate the volume from the time and the gas flow rate.

Notes

1. You must predispense a sufficient amount of buffer solution into the titration vessel to determine the water content of acid gases, e.g. hydrogen chloride.
2. If you titrate large quantities of gas in the same solvent, you should replace the evaporated methanol that has been lost in the gas stream depending on titration time and number of determinations (see Section 7.5, Note 5).
3. You cannot introduce $CO_2$ gas into the titration vessel directly, because iodine reacts with $CO_2$. The $CO_2$ gas must be directed through a water-dissolving, water-free absorption liquid in which $CO_2$ itself does not dissolve. The water contained in the gas is then absorbed by the liquid and can be determined by means of Karl Fischer titration in a process similar to external extraction (see Section 7.2).
4. **DL31/38**: Select "Max. time" and a "Delay" of 6000 s as termination parameters, to ensure that the titration is terminated after the maximum time.

# 8 Troubleshooting

| Problem | Possible causes and action to take |
|---|---|
| Titrated solution is dark yellow to brown instead of bright yellow | *Overtitration!*<br>Ð Clean platinum pins of the electrode with a paper towel. |
| Drift too high after pretitration of fresh solvent | *Titration stand not protected against moisture!*<br>Ð Replace molecular sieve and silica gel in the drying tube.<br>Ð Check whether titration stand is completely sealed (see Section 5.1.2). |
| Drift too high after titration of a sample (titration never ends, long titration time) | *The sample has not completely dissolved and continuously releases water!*<br>Ð Use longer mixing time or different solvent which dissolves the sample or extracts the water quicker.<br>*Side reaction of the sample with the KF reagent!*<br>Ð Use different method, e.g. external extraction, drying oven, etc. (see Sections 7.2 and 7.5). |
| Long titration time;<br>titration never ends | *Wrong termination parameters!*<br>Ð Use "Rel. drift stop" as a termination parameter.<br>Ð Increase value for relative drift stop (see Section 4.2.3).<br>Ð Increase end point if necessary (see Section 3.1.2). |
| Poor reproducibility of the results | *Amount of sample too small!*<br>Ð Increase amount of sample to ensure 10 mg water per sample (see Section 5.4.3).<br>*Water distribution in the sample not homogeneous!*<br>Ð Homogenize sample, if possible increase amount of sample (see Sections 5.4.5 and 7.2).<br>*Wrong control parameters!*<br>Ð Check and optimize control parameters (see Section 4.4).<br>*Wrong sample preparation and addition!*<br>Ð See Sections 5.4.4 and 5.4.5.<br>*Low water content (<1000 ppm)!*<br>With low water contents the reproducibility depends primarily on careful sample preparation and addition (see Sections 5.4.4 and 5.4.5). |

| **Problem** | **Possible causes and action to take** |
|---|---|
| Isolated values too low | *Titration terminated too early!*<br>Ð Reduce ΔVmin. Set a lower value for "Rel. drift stop"; reduce ΔVmax if necessary.<br>*Sample added incompletely!*<br>Ð Use back weighing method (see Sections 5.4.4 and 5.4.5). |
| Isolated values too high | *Control parameters too fast (= slight overtitration)*<br>Ð Reduce ΔVmax and ΔVmax factor (see Sections 4.4.2 and 4.4.3). |
| The results in a series change continuously (decreasing water content) | *Dissolving capacity of the solvent is exhausted!*<br>Ð Change solvent or use fresh solvent after every sample (see Section 5.3.2). |
| Very slow titration with two-component titrant | *No more sulfur dioxide in the solvent!*<br>Ð Change solvent (see Section 5.3.2). |
| Wrong or greatly fluctuating values in the concentration determination with water | *Water as standard requires practice!*<br>The use of water as a standard for the concentration determination requires skill and care to obtain reproducible and accurate results (see Section 5.2.4). Determination of the concentration using di-sodium tartrate or Water Standard 10.0 is a simpler and a more dependable method (see Sections 5.2.2 and 5.2.3). |
| Increasing value in the concentration determination with di-sodium tartrate | *di-sodium tartrate has only limited solubility!*<br>In methanol max. 0.12 g in 40 mL.<br>Ð Replace the solvent frequently. The concentration determination is correct only if the di-sodium tartrate has completely dissolved (see Section 5.2.2). |

## References

### *Cited literature*

[1] BUNSEN, R.W.: Liebigs Ann. Chem. **86**, 265 (1853)

[2] FISCHER, K. : Neues Verfahren zur massanalytischen Bestimmung des Wassergehaltes von FlŸssigkeiten und festen Kšrpern; Angew, Chem. **48**, 394 - 396 (1935)

[3] SMITH, D.M., W. M. BRYANT, J. MITCHELL jr.: Analytical Procedures Employing Karl Fischer Reagent I. Nature of the Reagent; J. Amer. Chem. Soc **61**, 2407 - 2412 (1939)

[4] VERHOFF, J.C., E. BARENDRECHT: Mechanism and reaction rate of the Karl Fischer titration reaction. Part I. Potentiometric measurements; J. Electronal. Chem. **71**, 305-315 (1976)

VERHOFF, J.C., E. BARENDRECHT: Mechanism and reaction rate of the Karl Fischer titration reaction. Part II. Rotating ring disk electrode meassurement; J. Electronal. Chem. **75**, 705-717 (1976)

VERHOFF, J.C., E. BARENDRECHT: Mechanism and reaction rate of the Karl Fischer titration reaction. Part V. Analytical implications; Anal. Chim. Acta. **94**, 395-403 (1977)

VERHOFF, J.C., W. Th. KOK: Mechanism and reaction rate of the Karl Fischer titration reaction. Part III. Rotating ring disk electrode meassurement - comparison with the aqueous system; J. Electronal. Chem. **86**, 407-415 (1978)

VERHOFF, J.C., W. P. COFINO: Mechanism and reaction rate of the Karl Fischer titration reaction. Part IV. First and second order catalytic currents at a rotating disk electrode; J. Electronal. Chem. **93**, 75-80 (1978)

[5] SCHOLZ, E.: Karl-Fischer Reagenzien ohne Pyridin; Fresenius Z. Anal. Chem., **303**, 203 - 207 (1980)

SCHOLZ, E.: Karl-Fischer Reagenzien ohne Pyridin; Genauigkeit der Wasserbestimmung; Fresenius Z. Anal. Chem., **306**, 394 - 396 (1981)

SCHOLZ, E.: Karl-Fischer Reagenzien ohne Pyridin; Einkomponenten Reagenzien; Fresenius Z. Anal. Chem., **309**, 30-32 (1981)

SCHOLZ, E.: Karl-Fischer Reagenzien ohne Pyridin; Neue Eichsubstanzen; Fresenius Z. Anal. Chem., **309**, 123-125 (1981)

SCHOLZ, E.: Karl-Fischer Reagenzien ohne Pyridin; Zweikomponenten-Reagenzien mit Imidazol; Fresenius Z. Anal. Chem., **312**, 460-464 (1982)

[6] SEUBERT, A.: Diplomarbeit an der UniversitŠt Hannover (1988)

[7] EBERIUS, E.: Wasserbestimmung mit Karl Fischer Lšsung; 2. Auflage, Verlag Chemie Weinheim (1954)

### *Additional literature*

- HYDRANAL ¨ -Praktikum: Wasserreagenzien fŸr die Karl-Fischer-Titration, Auflage 1992; Riedel-de Ha‘n D-30918 Seelze
- Karl-Fischer-Titration; E. Scholz, Springer Verlag Berlin 1984
- Wasserbestimmung durch Karl-Fischer-Titration: Theorie und Praxis; G. Wieland, GIT Verlag GmbH, Darmstadt (1985)
- SCH…FFSKI, K.: Untersuchungen einer Karl-Fischer-Reaktion; Diplomarbeit an der UniversitŠt Hannover (1989)

### *Standards*

ASTM E-700: Water in gases using Karl Fischer reagent
ASTM D-1364: Test method for water in volatile solvents (Karl Fischer titration)
ASTM D-1533: Water in insulating liquids (Karl Fischer method)
ASTM D-1744: Water in liquid petroleum products by Karl Fischer reagent
ASTM D-4017: Standard test method
ASTM D-4377: Test method for water in crude oil (Karl Fischer titration)
EN ISO 10101: Erdgas - Bestimmung des Wassergehaltes nach Karl Fischer
ISO 3699: Anhydrous hydrogen fluoride for industrial use - Determination of water content - Karl Fischer method
ISO 2097: Glycerols for industrial use - Determination of water content - Karl Fischer method
ISO 6191: Light olefins for industrial use - Determination of water content - Karl Fischer method
DIN 51777: PrŸfung von Mineralšl-Kohlenwasserstoffen und Lšsungsmitteln - Wasserbestimmung nach Karl Fischer
DIN 53515: Wasserbestimmung von pulverfšrmigen Kunststoffen nach Karl Fischer
DIN 53979: PrŸfung von Hilfsmitteln fŸr die Chemischreinigung - Wasserbestimmung nach Karl Fischer

## METTLER TOLEDO titrators

METTLER TOLEDO offers various titrators for the determination of water according to Karl Fischer.

### Special Karl Fischer titrators: DL31 and DL38

The most important features of these titrators are as follows:

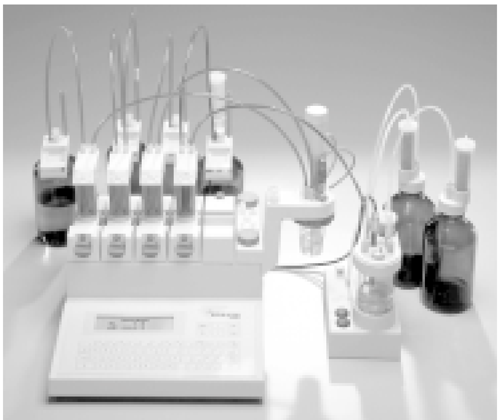
- Extremely well sealed titration stand: drift < 2 µg/min.
- Burette resolution of 10 000 steps.
- TTL inputs and outputs for controlling pumps, valves or mixers (DL38 only).
- Menu-driven dialog concept with 6-line display and command and function keys for simple communication with the titrator.
- Online help texts for functions and parameters.
- New: fuzzy logic control for fast and accurate water determinations according to Karl Fischer.
- Variable control parameters for water determinations in any sample matrix.
- Tutorial menu that guides you through the titrator installation procedure up to your first titration.
- Learn titration and titrant-specific control parameters for straightforward method development.
- Auto start parameter (DL38 only), i.e. the titration begins as soon as the titrator detects water.
- Auxiliary function for calculating the amount of sample on the basis of the expected water content.
- Integrated formulae for automatic determinations with samples that are extracted or dissolved externally (DL38 only).
- Documentation in accordance with GLP requirements and output of potential/time, volume/time and drift/time curves on an EPSON-compatible printer.
- Titrant list including batch number, current concentration, date of last concentration determination and expiry date for 20 different reagents (10 in the case of DL31).
- Computer connection for data transfer, remote control and reevaluation.
- Determination of the bromine number (DL38 only).

### General-purpose titrators: DL53, DL55 and DL58

In addition to general-purpose titrations, such as acid, base, precipitation and REDOX titrations, you can also use these titrators to perform Karl Fischer titrations. For this, you must install a KF option (for the voltametric indication) and a Karl Fischer titration stand (DV705).
The most important features of the titrators for Karl Fischer titrations are as follows:

- Separate, extremely well sealed titration stand: drift < 2 µg/min.
- Burette resolution of 5000 steps.
- TTL inputs and outputs for controlling pumps, valves or mixers.
- Menu-driven dialog concept with 6-line display and command and function keys for simple communication with the titrator.
- Continuous end point titration with fuzzy logic for fast and accurate Karl Fischer titrations.
- Variable control parameters for water determinations in any sample matrix.
- Three METTLER methods stored in the titrator for concentration, drift and sample determinations.

- Karl Fischer methods on memory card for automatic determinations with samples that are extracted or dissolved externally (DL58 only).
- Online titration curves: "potential vs. time" and "volume vs. time" (DL55 and DL58).
- Documentation in accordance with GLP requirements and output of potential/time and volume/time curves on an EPSON-compatible printer.
- Titrant list including current concentration, date of last concentration determination and expiry date for more than 100 different reagents.
- Computer connection for data transfer, remote control and reevaluation.



## General-purpose titrators: DL67, DL70ES and DL77

In addition to general-purpose titrations, such as acid, base, precipitation and REDOX titrations, you can also use these titrators to perform Karl Fischer titrations. For this, you must install a DK102A current source (for the voltametric indication) and a Karl Fischer titration stand (DV705).

The most important features of the titrators for Karl Fischer titrations are as follows:

- Separate, extremely well sealed titration stand: drift < 2µg/min.
- Burette resolution of 5000 steps.
- Menu-driven dialog concept with large, 7-line display for simple communication with the titrator.
- Variable control parameters for water determinations in any sample matrix.
- Four METTLER methods stored in the titrator for standby titration and for concentration, drift and sample determinations.
- Flexible method concept to facilitate automatic determinations with samples that are extracted or dissolved externally.
- Parallel titration (DL77 only): you can perform a Karl Fischer titration simultaneously with a general-purpose titration or keep the titration stand water-free with the standby titration.
- Online titration curves: "potential vs. time" and "volume vs. time".
- Documentation in accordance with GLP requirements and output of potential/time and volume/time curves on an EPSON-compatible printer.
- Titrant list including current concentration and date of last concentration determination for more than 100 different reagents.
- Computer connection for data transfer, remote control and reevaluation.

# Concentration determination with Water Standard 10.0

**Sample:** **Water Standard 10.0**

**Preparation:** --

**Sample introd.:** 10 mL syringe with needle

**Titrant:** One-component 5 mg $H_2O$/mL
(Hydranal¨ Composite 5 No. 34805)

**Solvent:** 40 mL methanol

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 900

**Accessories:** --

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26             V1.0                Titrator ID            A24
15-07-1998         14:16               User            V. Mueller
=================================================================

Conc. determination
-----------------------------------------------------------------
Method No.          900                Titrant           1-comp 5
01-06-1998         12:00               Burette               5 mL
Title       Standard 10
-----------------------------------------------------------------
15-07-1998         14:14               Speed [%]               35
Sample No.            1                Mix time [s]             0
Standard  H2O standard 10              Conc. (old)         5.0000
H2O content      10.000                Drift [µg/min]           1
Unit               mg/g                Consumpn [mL]       1.5685
Charge            72610                Duration [min]        1:21
Mass [g]         0.7728                Termination     Rel. drift

Conc. = 4.9286 mg/mL
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26             V1.0                Titrator ID            A24
15-07-1998         14:50               User            V. Mueller
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.          900                Title          Standard 10
01-06-1998         12:00

R1       n    = 4
         x̄    = 4.9234 mg/mL
         s    = 0.005612 mg/mL
         srel = 0.114 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 26              V1.0
15-07-1998         17:30
Titrator ID          A24
========================
Method
-----------------------
Method No.           900
01-06-1998         12:00
Title        Standard 10
------------------------
Sample parameters
  ID
  Type              Mass
  Minimum [g]     0.0000
  Maximum [g]     5.0000
  Entry           Before
Speed [%]             35
Mix time [s]           0
Titrant         1-comp 5
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         6.0
  ΔVmax factor [%]   100
  Start           Normal
Termination param.
  Max. time [s]      300
  Drift stop        Rel.
  Drift [µg/min]      15
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =           x[%]*f1
  f1 =            1.0000
  Unit                 %
  Decimal places       4
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

The Water Standard 10.0 is drawn out of the ampoule into a 10 mL syringe with a needle that has been rinsed beforehand with approximately 1 mL water standard. The standard is then injected into the KF titration vessel in portions of 1 mL to 1.5 mL and the weight determined by back weighing.
See Section 5.4.4.

Method 900 is a standard method, e.g. for the water determination in methanol. You must start the measurement by pressing <F2> "CONC" in the Analysis menu in order to determine the actual concentration of the titrant.

### Disposal

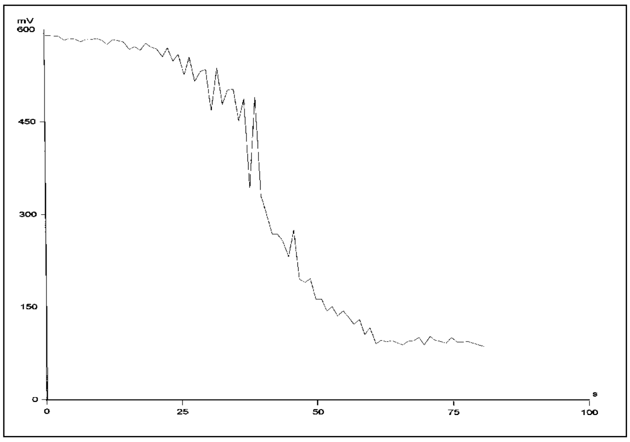
Organic wastes

### Other titrators

Application 900 also functions with the DL31.

Author: Viola Mueller-Schindler

## Curve



**METTLER TOLEDO** **Application No. M301**

# Concentration determination with di-sodium tartrate • 2 $H_2O$

**Sample:** **0.04 – 0.08 g di-sodium tartrate • 2 $H_2O$**

**Preparation:** Grind sample finely

**Sample introd.:** Weighing boat

**Titrant:** One-component 5 mg $H_2O$/mL
(Hydranal¨ Composite 5 No. 34805)

**Solvent:** 40 mL methanol

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 901

**Accessories:** --

**Indication:** DM143-SC

**Results**:

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26              V1.0                 Titrator ID          A24
15-06-1998         15:50                 User                  aa
=================================================================

Conc. determination
-----------------------------------------------------------------
Method No.           901                 Titrant         1-comp 5
01-06-1998         12:00                 Burette             5 mL
Title        Na tartrate
-----------------------------------------------------------------
15-06-1998         15:43                 Speed [%]             50
Sample No.             1                 Mix time [s]         120
Standard  di-Na tartrate                 Conc. (old)       5.0000
H2O-content       15.660                 Drift [µg/min]         3
Unit                   %                 Consumpn [mL]     1.8540
Charge             71470                 Duration [min]      4:04
Mass [g]         0.06250                 Termination   Rel. drift

Conc. = 5.2826 mg/mL
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26              V1.0                 Titrator ID          A24
15-06-1998         16:50                 User                  aa
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.           901                 Title        Na tartrate
01-06-1998         12:00

R1       n    = 7
         x̄    = 5.2954 mg/mL
         s    = 0.0073 mg/mL
         srel = 0.138 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 26              V1.0
15-05-1998         17:30
Titrator ID          A24
========================
Method
------------------------
Method No.           901
01-06-1998         12:00
Title        Na tartrate
------------------------
Sample parameters
  ID
  Type              Mass
  Minimum [g]     0.0000
  Maximum [g]     5.0000
  Entry           Before
Speed [%]             50
Mix time [s]         120
Titrant         1-comp 5
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         5.0
  ΔVmax factor [%]   100
  Start           Normal
Termination param.
  Max. time [s]      300
  Drift stop        Rel.
  Drift [µg/min]      15
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =           x[%]*f1
  f1 =            1.0000
  Unit                 %
  Decimal places       2
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

A mixing time of at least 120 s is required to ensure that the finely ground di-sodium tartrate is completely dissolved.

Di-sodium tartrate which is not finely ground needs a significantly longer mixing time.

The di-sodium tartrate must be completely dissolved (clear solution) in order to guarantee correct results.

A cloudy solution means incorrect results (too high). In this case the solvent must be changed. The solvent should always be replaced after two or three samples. See also Section 5.2.2.

When adding di-sodium tartrate with the weighing boat, you must make sure that none of it adheres to the beaker wall or to the electrode. A weighing boat with a flexible tube is useful here. See Section 5.4.5.

Method 901 is a standard method, e.g. for the water determination in methanol. You must start the measurement by pressing <F2> "CONC" in the Analysis menu to determine the actual concentration of the titrant and **change the mixing time from 10 to 120 s**.

### Disposal

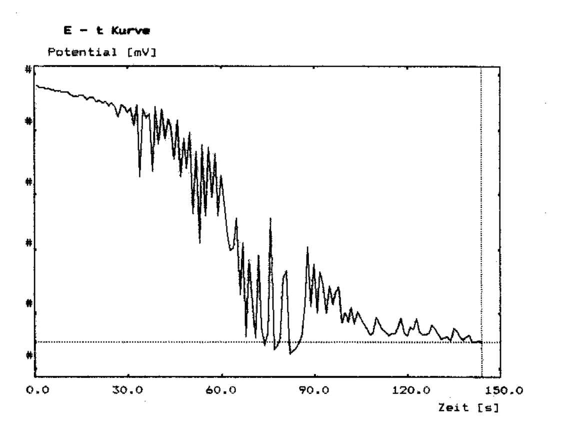
Organic wastes

### Other titrators

Application 901 also functions with the DL31.

Author: A. Aichert

## Curve



# METTLER TOLEDO Application No. M302

## Water determination in solvents

**Sample:** **Dry toluene**

**Preparation:** --

**Sample introd.:** 10 mL syringe with needle

**Titrant:** One-component 2 mg $H_2O$/mL
(Hydranal¨ Composite 2  No. 34806)

**Solvent:** 40 mL methanol

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 902

**Accessories.:** --

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26              V1.0                  Titrator ID         A24
29-07-1998         16:26                  User         V. Mueller
=================================================================

KF determination
-----------------------------------------------------------------
Method No.           902                  Titrant.       1-comp 2
01-06-1998         12:00                  Conc. [mg/mL]    2.1403
Title        Toluene dry                  Burette            5 mL
-----------------------------------------------------------------
29-07-1998         16:15                  Wait time [s]         0
Sample No.             1                  Blank [µg]            0
ID               Toluene                  Drift [µg/min]        1
Mass [g]           3.391                  Consumpn [mL]    0.2190
Speed [%]             35                  Duration [min]     2:05
Mix time [s]           0                  Termination   Rel. drift
Predisp.  [mL]    0.0000


f1 = 1.0000
R1 = 137.612 ppm
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26              V1.0                  Titrator ID         A24
29-07-1998         17:51                  User         V. Mueller
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.           902                  Title       Toluene dry
01-06-1998         12:00

R1       n    = 4
         x̄    = 138.191 ppm
         s    = 2.451 ppm
         srel = 1.774 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 26              V1.0
29-07-1998         18:05
Titrator ID          A24
========================
Method
------------------------
Method No.           902
01-06-1998         12:00
Title        Toluene dry
------------------------
Sample parameters
  ID             Toluene
  Type              Mass
  Minimum [g]     3.0000
  Maximum [g]     8.0000
  Entry           Before
Speed [%]             35
Mix time [s]           0
Titrant         1-comp 2
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         4.0
  ΔVmax factor [%]   100
  Start         Cautious
Termination param.
  Max. time [s]      300
  Drift stop        Rel.
  Drift [µg/min]      10
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =         x[ppm]*f1
  f1 =            1.0000
  Unit               ppm
  Decimal places       3
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

The sample is drawn in with a 10 mL syringe with a needle. It is then injected into the KF titration vessel in portions of 3 mL to 8 mL and the weight determined by back weighing. If the amount of water involved is very small, the titration can also be started with the parameter "Cautious".
See also Section 4.1.3.

### Disposal

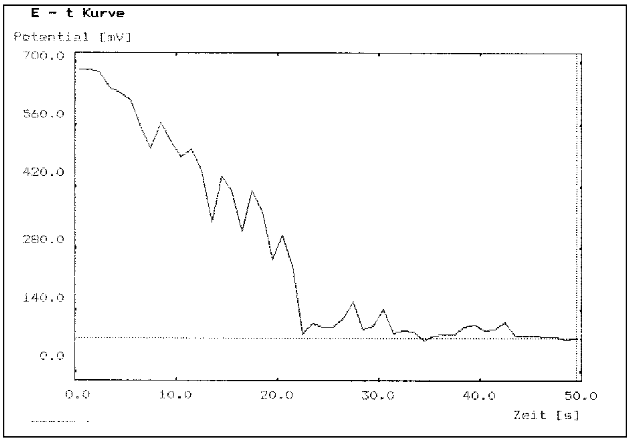
Organic wastes

### Other titrators

Application 902 also functions with the DL31.

Author: Viola Mueller-Schindler

## Curve



# Water determination in ketones

**Sample:** Acetone

**Preparation:** --

**Sample introd.:** Syringe

**Titrant:** One-component 5 mg $H_2O$/mL
(Hydranal¨ Composite 5K No. 34816)

**Solvent:** 40 mL

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 903

**Accessories:** --

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 04             V1.0                Titrator ID            A24
27-07-1998         10:03               User               J. Maag
=================================================================

KF determination
-----------------------------------------------------------------
Method No.          903                Titrant          1-comp 5K
01-06-1998         12:00               Conc. [mg/mL]       4.7821
Title             Ketone               Burette               5 mL
-----------------------------------------------------------------
27-07-1998         10:06               Wait time [s]            0
Sample No.             1               Blank [µg]               0
ID               Acetone               Drift [µg/min]           3
Mass [g]          2.0598               Consumpn [mL]       0.5930
Speed [%]             35               Duration [min]        1:42
Mix time [s]          10               Termination     Rel. drift
Predisp.  [mL]    0.0000

f1 = 1.0000
R1 = 1374.26 ppm
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 4               V1.0                Titrator ID           A24
27-07-1998         11:05                User              J. Maag
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.           903                Title              Ketone
01-06-1998         12:00

R1       n    = 5
         x̄    = 1373.65 ppm
         s    = 3.060134 ppm
         srel = 0.223 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 04              V1.0
27-07-1998         10:03
Titrator ID          A24
========================
Method
------------------------
Method No.           903
01-06-1998         12:00
Title             Ketone
------------------------
Sample parameters
  ID             Acetone
  Type              Mass
  Minimum [g]     0.0000
  Maximum [g]     5.0000
  Entry           During
Speed [%]             35
Mix time [s]          10
Titrant        1-comp 5K
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     125
  ΔVmin [µL]         0.5
  ΔVmax [µL]         6.0
  ΔVmax factor [%]   100
  Start           Normal
Termination param.
  Max. time [s]      300
  Drift stop        Rel.
  Drift [µg/min]      10
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =         x[ppm]*f1
  f1 =            1.0000
  Unit               ppm
  Decimal places       2
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

### Control parameters

Since the end point depends on the solvent, it had to be increased from 100 mV (default value) to 125mV.

### Procedure

In the normal Karl Fischer reagents, ketones and aldehydes form ketals and acetals, whereby water is produced. This falsifies the results of the water content deter-mination. Methanol-free reagents are therefore used for the Karl Fischer titration with acetone. (Hydranal¨ Composite 5K as the titrant, Hydranal¨ Working medium K as the solvent).
You must wait for a constant drift value (approx. five minutes) after each titration for the side reactions to subside.
The solvent must be replaced after every 3 to 5 samples, depending on the sample amount.

### Disposal

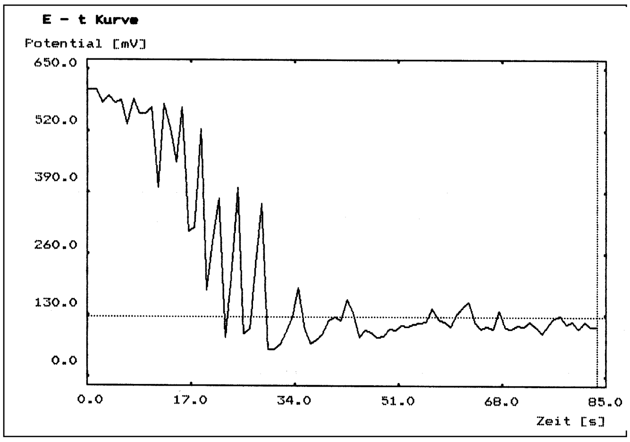
Organic wastes

### Other titrators

Application 903 also functions with the DL31.

Author: J. Maag

## Curve



# Water determination with internal extraction (homogenizer)

**Sample:** **Powdered milk**

**Preparation:** --

**Sample introd.:** Weighing boat

**Titrant:** One-component 5 mg $H_2O$/mL
(Hydranal¨ Composite 5  No. 34806)

**Solvent:** 100 mL

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 904

**Accessories:** TBox DR42 / homogenizer
Special cover for titration stand

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 1              V1.0                Titrator ID            AL1
15-07-1998        15:24                User            Reto Huber
=================================================================

KF determination
-----------------------------------------------------------------
Method No.          904                Titrant           1-comp 5
01-06-1998        12:00                Conc. [mg/mL]       4.0010
Title       Homogenizer                Burette               5 mL
-----------------------------------------------------------------
15-07-1998        15:37                Wait time [s]            0
Sample No.            4                Blank [µg]               0
ID                                     Drift [µg/min]          13
Mass [g]        0.17407                Consumpn [mL]       1.1150
Speed [%]            50                Duration [min]        2:01
Mix time [s]         60                Termination     Rel. drift
Predisp.  [mL]   0.0000

f1 = 1.0000
R1 = 2.55 %
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 1              V1.0                Titrator ID            AL1
15-07-1998        15:43                User            Reto Huber
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.          904                Title          Homogenizer
01-06-1998        12:00

R1       n    = 5
         x̄    = 2.54 %
         s    = 0.02 %
         srel = 0.885 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 1               V1.0
15-07-1998         15:21
Titrator ID          AL1
========================
Method
------------------------
Methodn Nr.          904
01-06-1998         12:00
Title        Homogenizer
------------------------
Sample parameters
  ID
  Type              Mass
  Minimum [g]     0.1000
  Maximum [g]     0.5000
  Entry           During
Speed [%]             50
Mix time [s]          60
Titrant         1-comp 5
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start           Yes
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         8.0
  ΔVmax factor [%]   100
  Start           Normal
Termination param.
  Max. time [s]      240
  Drift stop        Rel.
  Drift [µg/min]      15
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =           x[%]*f1
  f1 =            1.0000
  Unit                 %
  Decimal places       2
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

This method allows an easy and fast water determination of powdered milk or of other solid, insoluble samples. The homogenizer starts reducing the sample automatically as soon as it is added; the amount of sample is entered subsequently during the titration.

### Homogenizer

The homogenizer is controlled by the TBox and is permanently mounted in the titration stand. A special cover is needed for the titration vessel as well as an adapter. The homogenizer, the cover and the adapter can be ordered from MSG AnaChem.

There must be a sufficient amount of methanol (100 mL) in the titration vessel, because the solvent acts as a lubricant for the homogenizer. The homogenizer must never be operated "dry".

### Stirring speed and mixing time

The stirring speed must be fast enough to ensure thorough mixing.

The "Mix time" parameter corresponds to the homogenizing time. You should select a mixing time of 120 s for large sample amounts or for large grain sizes.

The mixing time is too short if a very high drift persists for a long time after the titration is terminated.

### Control and termination parameters

ΔVmax should be reduced to 5.0 µL if there is a risk of overtitration.

The relative drift stop should be set to 40 µg/min for samples that only release water very slowly (see Section 4.4.5).

### Disposal

Organic wastes

### Other titrators

Application 904 only functions with the DL38.

Author: Reto Huber

**METTLER TOLEDO** **Application No. M305**

# Water determination with external extraction

**Sample:** **Curry**

**Preparation:** External extraction in methanol

**Sample introd.:** 10 mL syringe with needle

**Titrant:** One-component 5 mg $H_2O$/mL
(Hydranal¨ Composite 5  No. 34806)

**Solvent:** 40 mL methanol

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 905

**Accessories:** --

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26              V1.0                Titrator ID           A24
29-07-1998         14:42                User           V. Mueller
=================================================================

KF determination
-----------------------------------------------------------------
Method No.           905                Titrant          1-comp 5
01-06-1998         12:00                Conc. [mg/mL]      4.9234
Title         Ext. Extr.                Burette              5 mL
-----------------------------------------------------------------
29-07-1998         14:40                Wait time [s]           0
Sample No.             1                Blank [µg]              0
ID                 Curry                Drift [µg/min]          3
Mass [g]          3.3645                Consumpn [mL]      2.5510
Speed [%]             35                Duration [min]       3:25
Mix time [s]           0                Termination    Rel. drift
Predisp.  [mL]    0.0000

f1 = 0.0127
f2 = 68.3078
f3 = 4.1496
R1 = 5.9388 %
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 26               V1.0                Titrator ID          A24
29-07-1998          15:21                User          V. Mueller
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.            905                Title         Ext. Extr.
01-06-1998          12:00

R1      n     = 5
        x̄     = 5.9401 %
        s     = 0.00735 %
        srel = 0.124 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 26              V1.0
29-07-1998         14:36
Titrator-ID          A24
========================
Method
------------------------
Method No.           905
01-06-1998         12:00
Title         Ext. Extr.
------------------------
Sample parameters
  ID               Curry
  Type              Mass
  Minimum [g]     2.0000
  Maximum [g]     5.0000
  Entry           Before
Speed [%]             35
Mix time [s]           0
Titrant         1-comp 5
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         6.0
  ΔVmax factor [%]   100
  Start           Normal
Termination param.
  Max. time [s]      300
  Drift stop        Rel.
  Drift [µg/min]      15
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =     x[%]ext.extr.
  f1 =            0.0127
  f2 =           68.3078
  f3 =            4.1496
  Unit                 %
  Decimal places       4
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output   Print.+Comp.
  Type               GLP
```

## Remarks

The water content of the solvent (methanol) is determined first and entered in the calculation as factor 1. Next, the weight of the solvent is entered in the calculation as factor 2. The sample to be extracted is then added to the solvent and the sample weight (curry) entered in the calculation as factor 3. You must select "No calculation" for calculations 2 and 3.

The solvent and the sample are left to stand for a while until all the water is extracted. The extraction can be speeded up by shaking.

The clear solution is then injected into the KF titration vessel using a syringe with a needle and the weight determined by back weighing.

The weight of the extracted sample should be as large as possible in relation to the solvent, to ensure that the dilution factor is not too high. You must however take account of the saturation limit of all solvents with regard to water.

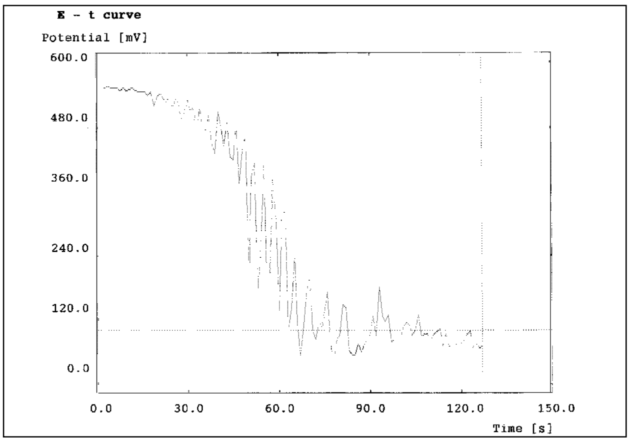
See also Section 7.2.

### Disposal

Organic wastes

Author: Viola Mueller-Schindler

## Curve



# Water determination in PET granules

**Sample:** **1 – 3 g PET granules**

**Preparation:** --

**Sample introd.:** Sample boat for KF oven

**Titrant:** One-component 5 mg $H_2O$/mL
(Hydranal¨ Composite 5  No. 34805)

**Solvent:** 40 mL methanol

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 906

**Accessories:** DO305 KF oven

**Indication:** DM143-SC DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 25              V1.0                Titrator ID          I 25
17-07-1998         11:26                User           C. De Caro
=================================================================

KF determination
-----------------------------------------------------------------
Method No.           906                Titrant          1-comp 5
01-06-1998         12:00                Conc. [mg/mL]      5.1402
Title            KF Oven                Burette              5 mL
-----------------------------------------------------------------
17-07-1998         11:34                Wait time [s]           0
Sample No.             2                Blank [µg]              0
ID                                      Drift [µg/min]          1
Mass [g]          1.3612                Consumpn [mL]      0.0305
Speed [%]             35                Duration [min]      10:44
Mix time [s]         600                Termination    Rel. drift
Predisp. [mL]     0.0000

f1 = 1.0000
R1 = 0.0107 %
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 25              V1.0                  Titrator ID        I 25
17-07-1998         18:36                  User         C. De Caro
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.           906                  Title           KF Oven
01-06-1998         12:00

R1      n    = 6
        x̄    = 0.0115 %
        s    = 0.000752 %
        srel = 6.557 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 25              V1.0
17-07-1998         18:37
Titrator ID         I 26
========================
Method
------------------------
Method No.           906
01-06-1998         12:00
Title           KF Oven
------------------------
Sample parameters
  ID
  Type              Mass
  Minimum [g]     1.0000
  Maximum [g]     3.0000
  Entry           Before
Speed [%]             35
Mix time [s]         600
Titrant         1-comp 5
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         5.0
  ΔVmax factor [%]   100
  Start         Cautious
Termination param.
  Max. time [s]      240
  Drift stop        Rel.
  Drift [µg/min]      15
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =           x[%]*f1
  f1 =            1.0000
  Unit                 %
  Decimal places       4
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

1) The oven is purged with nitrogen gas that has been dried with molecular sieve. The flow rate of the gas should be such that the bubbles in the solvent are easily visible inside the titration vessel.

2) The oven is heated to 280 °C prior to the measurement and purged with nitrogen gas until the required temperature is reached and the drift value is both low and stable (approx. 5 µg/min). The sample boat is inserted into the hot zone of the oven in order to evaporate the moisture.

3) The sample melts and adheres to the boat when cold. The boat is therefore lined with aluminum foil, so that it can be cleaned without difficulty.

### Disposal

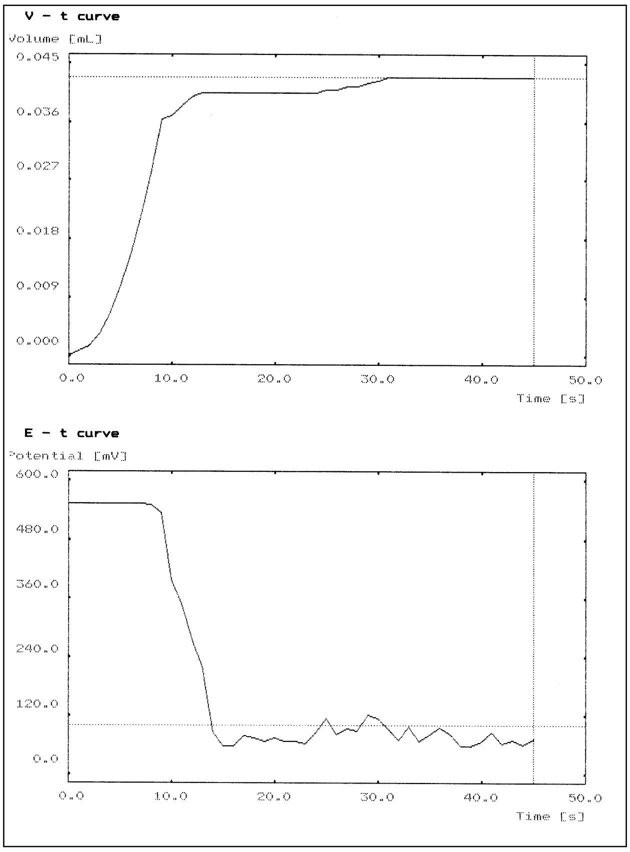
Organic wastes

### Other titrators

Application 906 also functions with the DL31.

Author: C. De Caro

## Curves



**METTLER TOLEDO** **Application No. M307**

# Water determination in gases

**Sample:** **Air**

**Preparation:** --

**Sample introd.:** With air pump via flowmeter into titration cell

**Titrant:** One-component 2 mg $H_2O$/mL
(Hydranal¨ Composite 2 No. 34806)

**Solvent:** 40 mL methanol

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 907

**Accessories:** Inlet tube ME-105091
Rotameter 0 Ð 120 mL/min

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 04             V1.0                Titrator ID            A24
29-07-1998        17:26                User                    aa
=================================================================

KF determination
-----------------------------------------------------------------
Method No.          907                Titrant           1-comp 2
01-06-1998        12:00                Conc. [mg/mL]       2.1403
Titel               Gas                Burette               5 mL
-----------------------------------------------------------------
17-07-1998        17:45                Predisp.  [mL]      0.0000
Sample No.            1                Wait time [s]            0
ID                  Air                Blank [µg]               0
Volume [mL]       0.610                Drift [µg/min]           1
Density [g/mL]    1.141                Consumpn [mL]       0.9115
Speed [%]            55                Duration [min]       11:16
Mix time [s]         60                Termination       Max.time

f1 = 1.0000
R1 = 2786.77 ppm
f2 = 1.1410
R2 = 3179.70 µg/L
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 04              V1.0                Titrator ID           A24
29-07-1998         18:50                User                   aa
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.           907                Title                 Gas
01-06-1998        12:00

R1       n    = 7
         x̄    = 2760.89 ppm
         s    = 86.17358 ppm
         srel = 2.121 %
```

## Method

```
========================
Method              DL38
------------------------
Method No.           907
01-06-1998         12:00
Title                Gas
------------------------
Sample parameters
  ID                 Air
  Type            Volume
  Density [g/ml]   1.141
  Minimum [ml]     0.000
  Maximum [ml]    999.00
  Entry           During
Speed [%]             55
Mix time [s]          60
Titrant         1-comp 2
Predisp. [mL]     0.0000
Wait time [s]          0
Auto start            No
Control parameters
  Current [µA]        20
  End point [mV]     100
  ΔVmin [µL]         0.5
  ΔVmax [µL]         5.0
  ΔVmax factor [%]   100
  Start         Cautious
Termination param.
  Max. time [s]      600
  Drift stop          No
  Delay [s]         6000
  Vmax [mL]       10.000
Blank [µg]             0
Drift             Online
Calculation 1
  R1 =         x[ppm]*f1
  f1 =            1.0000
  Unit               ppm
  Decimal places       2
  Statistics         Yes
  Max. srel [%]    0.000
Calculation 2
  R2 =        x [ppm]*f2
  f2 =            1.1410
  Unit              µg/L
  Decimal places       2
  Statistics          No
  Max srel. [%]     0.00
Calculation 3
Standby              Yes
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

The air is introduced into the titration vessel via an inlet tube and a flowmeter (see diagram in Section 7.6).

### Sample parameters

The density of the air under test conditions is entered, to allow the result to be calculated in ppm; 1.141 g/L at 20 °C and 95.7 kPa. Since the density is entered in g/L, the volume must also be entered in liters.

### Results

The water content in ppm is converted to µg/L in calculation 2 using the density.

### Procedure

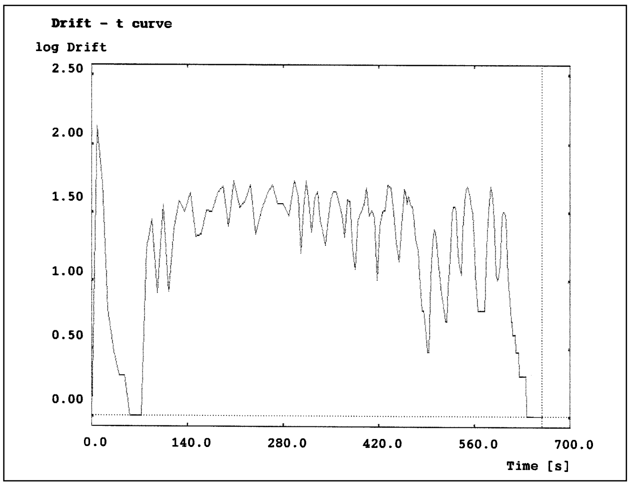
The system must be purged with the gas (air) prior to the determination.
When the drift is stable, start the titration and direct the gas stream through the titration vessel at a rate of 50 mL/min. The gas stream must be stopped after exactly 10 minutes. The volume of gas that has flown through the vessel is entered in liters.

### Disposal

Organic wastes

Author: A. Aichert

## Curve



**METTLER TOLEDO** **Application No. M308**

# Determination of the bromine number

**Sample:** **Approx. 0.3 g gasoline, 98 octane**

**Sample introd.:** Syringe

**Titrant:** Bromide-bromate solution
c(Br$_2$) = 0.05 mol/L
(e.g. from Merck, Titrisol bromide-bromate solution c(Br$_2$) = 0.05 mol/L )

**Solvent:** 50 mL bromine number solvent

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 908

**Accessories:** Thermostatable beaker
ME-51107497

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 24              V1.0                Titrator ID          I 24
16-07-1998         15:20                User          C. De Caro
=================================================================

Br No. determination
-----------------------------------------------------------------
Method No.                                                    908
01-06-1998                                                  12:00
Title                                                 Bromine No.
-----------------------------------------------------------------
16-07-1998            15:20              Wait time [s]          0
Sample No.                3              Blank [mmol]      0.0037
ID                98 Octane              Consumpn [mL]     2.5670
Mass [g]             0.1924              Duration [min]      7:23
Speed [%]                30              Termination        Delay
Mix time [s]            120
Predisp. [mL]        0.0000

f1 = 1.0000
Bromine No.  = 10.66
f2 = 1.0000
R2 = 2.567 mL
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 24              V1.0                Titrator ID          I 24
16-07-1998         18:02                User          C. De Caro
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.            908                Title        Bromine No.
01-06-1998          12:00

R1       n    = 9
         x̄    = 10.43
         s    = 0.300376
         srel = 2.881 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 24              V1.0
16-07-1998         15:04
Titrator ID         I 24
========================
Method
------------------------
Method No.           908
01-06-1998         12:00
Title        Bromine No.
------------------------
Sample parameters
  ID             Request
  Type              Mass
  Minimum [g]     0.2000
  Maximum [g]     0.4000
  Entry           Before
Speed [%]             30
Mix time [s]         120
Titrant         Br-/BrO3-
Predisp. [mL]     0.0000
Wait time [s]          0
Control parameters
  Current [µA]         1
  End point [mV]     150
  ΔVmin [µL]         1.0
  ΔVmax [µL]        20.0
  ΔVmax factor [%]   100
  Start           Normal
Termination param.
  Max. time [s]     6000
  Delay [s]           15
  Vmax [mL]       20.000
Blank [mmol]     Request
Calculation 1
  R1 =      x[Br No.]*f1
  f1 =            1.0000
  Unit
  Decimal places       2
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
  R2 =         x [mL]*f2
  f2 =            1.0000
  Unit                mL
  Decimal places       3
Statistics            No
Max strel. [%]      0.00
Calculations 3
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

1) This application describes the determination of the bromine number in accordance with ASTM Standard 1159-93. Since only small increments are added, the delay has been reduced from 30 s to 15s.

2) The determination is performed at a temperature between 0 and 5 °C. This temperature has been set to 3 °C by means of a thermostatable beaker.

### Solvent preparation

1 L of solvent is prepared as follows: 714 mL glacial acetic acid, 134 mL 1,1,1-trichloroethane, 134 mL ethanol and 18 mL $H_2SO_4$ (16%).

### Titrant preparation

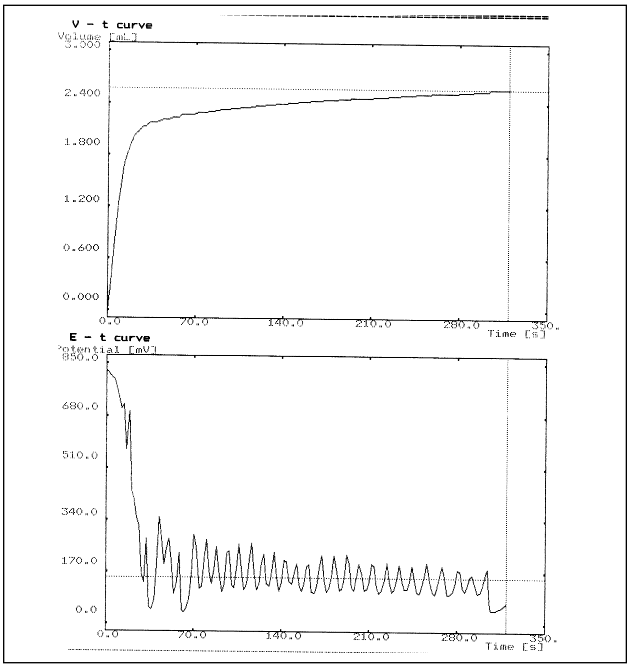
Commercial bromide-bromate solutions can be obtained from Merck (Titrisol, No. 109905) or from Fluka (bromine concentrate, No. 16053). The titrant can be prepared as follows: 10.2 g potassium bromide (KBr) and 2.784 g potassium bromate ($KBrO_3$) are dissolved in a 1 L volumetric flask with deionized water and filled up to the mark. The two salts must first be dried in the oven at 105 °C.

### Disposal

Non-aqueous, halogenated wastes

Author: C. De Caro

## Curves



**METTLER TOLEDO** **Application No. M309**

# Blank value for the bromine number determination

**Sample:** **50 mL bromine number solvent**

**Sample introd.:** 50 mL pipette

**Titrant:** Bromide-bromate solution
c(Br$_2$) = 0.05 mol/L
(e.g. from Merck, Titrisol bromide-bromate solution c(Br$_2$) = 0.05 mol/L )

**Solvent:** 50 mL bromine number solvent

**Instruments:** METTLER TOLEDO DL38
EPSON dot matrix printer

**Method:** 909

**Accessories:** Thermostatable beaker
ME-51107497

**Indication:** DM143-SC

**Results:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 24              V1.0                Titrator ID          I 24
16-07-1998         11:59                User          C. De Caro
=================================================================

Br No. determination
-----------------------------------------------------------------
Method No.                                                    909
01-06-1998                                                  12:00
Title                                                Blank Br No.
-----------------------------------------------------------------
16-07-1998         11:56                 Predisp. [mL]    0.0000
Sample No.             6                 Wait time [s]         0
ID                     1                 Consumpn [mL]    0.0720
Volume [mL]           50                 Duration [min]     3:22
Density [g/mL]     1.000                 Termination       Delay
Speed [%]             30
Mix time [s]         120

f1 = 0.0500
R1 = 0.0036 mmol
-----------------------------------------------------------------
```

**Statistics:**

```
=================================================================
METTLER TOLEDO                                               DL38
-----------------------------------------------------------------
SRN 24              V1.0                Titrator ID          I 24
16-07-1998         14:16                User          C. De Caro
=================================================================

Statistics report
-----------------------------------------------------------------
Method No.           909                 Title      Blank Br No.
01-06-1998         12:00

R1      n    = 6
        x̄    = 0.0037 mmol
        s    = 0.000055 mmol
        srel = 1.501 %
```

## Method

```
========================
METTLER TOLEDO      DL38
------------------------
SRN 24              V1.0
16-07-1998         14:18
Titrator ID         I 24
========================

Method
------------------------
Method No.           909
01-06-1998         12:00
Title       Blank Br No.
------------------------
Sample parameters
  ID             Request
  Type      Fixed volume
  Density [g/mL]   1.000
  Volume [mL]         50
Speed [%]             30
Mix time [s]         120
Titrant        Br-/BrO3-
Predisp. [mL]     0.0000
Wait time [s]          0
Control parameters
  Current [µA]         1
  End point [mV]     150
  ΔVmin [µL]         1.0
  ΔVmax [µL]         5.0
  ΔVmax factor [%]   100
  Start         Cautious
Termination param.
  Max. time [s]     6000
  Delay [s]           15
  Vmax [mL]       10.000
Blank [mmol]      0.0000
Calculation 1
  R1 =          x[mL]*f1
  f1 =            0.0500
  Unit              mmol
  Decimal places       4
  Statistics         Yes
  Max. srel [%]     0.00
Calculation 2
Calculation 3
Report
  Output    Print.+Comp.
  Type               GLP
```

## Remarks

1) This application describes the determination of the blank value for the bromine number determination in accordance with ASTM Standard 1159-93. Since only very small increments are added, the delay has been reduced from 30 s to 15s in order to shorten the titration time.

2) The determination is carried out between 0 and 5 °C. The temperature has been set to 3 °C for this application by means of a thermostatable beaker.

3) In order to obtain the unit mmol for the blank value, the consumption (mL) must be multiplied by the titrant concentration (mol/L). The factor f1 has therefore been set to a value of 0.05.

### Solvent preparation

1 L of solvent is prepared as follows: 714 mL glacial acetic acid, 134 mL 1,1,1-trichloroethane, 134 mL ethanol and 18 mL $H_2SO_4$ (16%).

### Titrant preparation

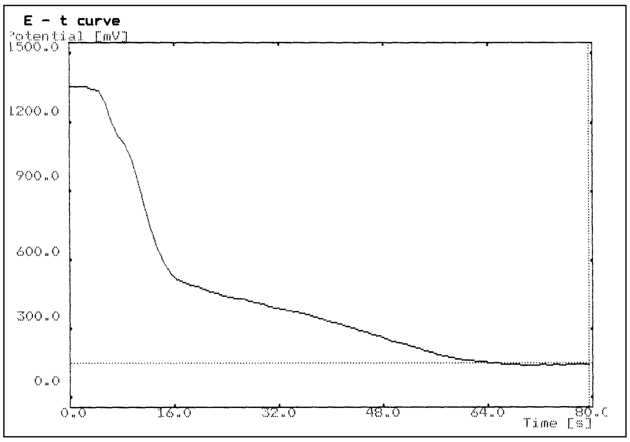
Commercial bromide-bromate solutions can be obtained from Merck (Titrisol, No. 109905) or from Fluka (bromine concentrate, No. 16053). The titrant can be prepared as follows: 10.2 g potassium bromide (KBr) and 2.784 g potassium bromate ($KBrO_3$) are dissolved in a 1 L volumetric flask with deionized water and filled up to the mark. The two salts must first be dried in the oven at 105 °C.

### Disposal

Non-aqueous, halogenated wastes

Author: C. De Caro

## Curve



Mettler-Toledo GmbH
Analytical
CH-8603 Schwerzenbach, Schweiz
Telefon (01) 806 77 11, Fax (01) 806 73 50
Internet: http://www.mt.com

AT Mettler-Toledo GmbH., A-1100 Wien
Tel. (01) 604 19 80, Fax (01) 604 28 80
AU Mettler-Toledo Ltd., Port Melbourne, Victoria 3207
Tel. (03) 9 644 5700, Fax (03) 9 645 39 35
BE N.V. Mettler-Toledo s.a., B-1651 Lot
Tel. (02) 334 02 11, Fax (02) 378 16 65
CH Mettler-Toledo (Schweiz) AG, CH-8606 Greifensee
Tel. (01) 944 45 45, Fax (01) 944 45 10
CN Mettler-Toledo (Shanghai) Ltd., Shanghai 200233
Tel. (21) 6485 04 35, Fax (21) 6485 33 51
CZ Mettler-Toledo, spol, s.r.o., CZ-12000 Praha 2
Tel. (02) 25 49 62, Fax (02) 242 475 83
DE Mettler-Toledo GmbH, D-35353 Giessen
Tel. (0641) 50 70, Fax (0641) 507 128
DK Mettler-Toledo A/S, DK-2600 Glostrup
Tel. (43) 270 800, Fax (43) 270 828
ES Mettler-Toledo S.A.E., E-08038 Barcelona
Tel. (03) 223 22 22, Fax (03) 223 02 71
FR Mettler-Toledo s.a., F-78222 Viroflay
Tel. (01) 309 717 17, Fax (01) 309 716 16
HK Mettler-Toledo (HK) Ltd., Kowloon
Tel. (02) 744 12 21, Fax (02) 744 68 78
HR Mettler-Toledo, d.o.o., HR-10000 Zagreb
Tel. (01) 230 41 47, Fax (01) 233 63 17
HU Mettler-Toledo, KFT, H-1173 Budapest
Tel. (01) 257 70 30, Fax (01) 257 21 75
IT Mettler-Toledo S.p.A., I-20026 Novate Milanese
Tel. (02) 333 321, Fax (02) 356 29 73
JP Mettler-Toledo K.K., Yokohama 231
Tel. (45) 633 53 50, Fax (45) 664 96 50
KR Mettler-Toledo (Korea) Ltd., Seoul (135-090)
Tel. (02) 518 20 04, Fax (02) 518 08 13
KZ Mettler-Toledo CA, 480009 Almaty
Tel. (07) 3272 608 834, Fax (07) 3272 608 835
MY Mettler-Toledo (M) Sdn. Bhd., 47301 Petaling Jaya
Tel. (03) 703 27 73, Fax (03) 703 17 72
MY Mettler-Toledo (S.E.A.), 47301 Petaling Jaya
Tel. (03) 704 17 73, Fax (03) 703 17 72
MX Mettler-Toledo S.A. de C.V., México C.P. 06430
Tel. (05) 547 57 00, Fax (05) 541 22 28
NL Mettler-Toledo B.V., NL-4000 HA Tiel
Tel. (0344) 638 363, Fax (0344) 638 390
PL Mettler-Toledo, Sp. z o.o., PL-02-929 Warszawa
Tel. (22) 651 92 32 Fax (22) 651 71 72
RU Mettler-Toledo C.I.S. AG, 10 1000 Moskau
Tel. (95) 921 92 11, Fax (95) 921 63 53
SE Mettler-Toledo AB, S-12008 Stockholm
Tel. (08) 702 50 00, Fax (08) 642 45 62
SG Mettler-Toledo (S) Pte. Ltd., Singapore 139944
Tel. 7 786 779, Fax 7 764 904
SK Mettler-Toledo, SK-83103 Bratislava
Tel. (07) 522 74 96, Fax (07) 237 190
SI Mettler-Toledo, d.o.o., SL-1236 Trzin
Tel. (06) 116 218 01, Fax (06) 116 217 89
TH Mettler-Toledo (Thailand) Ltd., Bangkok 10310
Tel. (02) 719 64 80, Fax (02) 719 64 79
TW Mettler-Toledo Pac Rim AG, Taipei
Tel. (2) 2579 59 55, Fax (2) 2579 59 77
UK Mettler-Toledo Ltd., Leicester, LE4 1AW
Tel. (0116) 235 70 70, Fax (0116) 236 63 99
US Mettler-Toledo, Inc., Worthington, OH 43085
Tel. (614) 438 4511, Fax (614) 438 4900

For all other countries:
Mettler-Toledo GmbH
PO Box, VI-400, CH-8606 Greifensee, Schweiz
Tél. (01) 944 22 11, Fax (01) 944 31 70

Subject to technical changes

Printed in Switzerland on 100% chlorine-free
paper, for the sake of our environment.