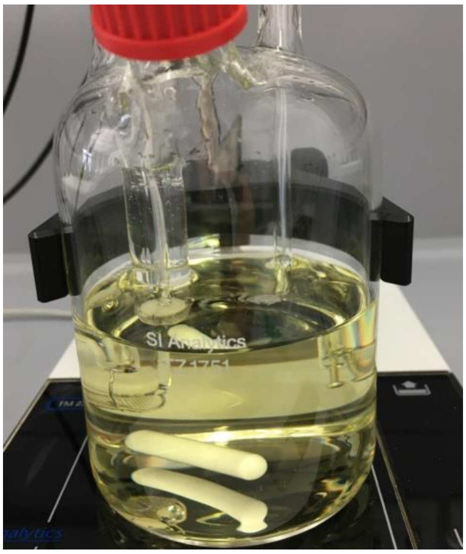
Coulometric KF-Titration Troubleshooting

Description

The coulometric Karl Fischer titration is a very pleasant thing for the user: the sample is injected into the titration cell, after the end of the titration the system is immediately ready for the next sample. In normal operation - except when changing the reagent - the user has no direct contact with the chemicals.
But what if it doesn't work as it should? In this guide, we describe the most common errors that can occur with coulometric KF titrations and how to resolve them.

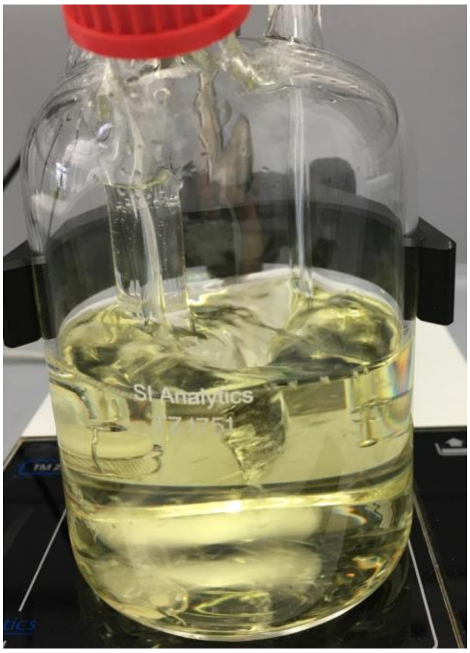
Basics

The titration cell must be sufficiently filled with the reagent so that the poles of the generator and indicator electrodes are completely covered by liquid. The best ammount for the TZ 1751 and TZ 1754 titration cells is approx. 140 ml. The liquid level should be between the label SI Analytics and TZ 1751 or TZ 1754.



When using a generator electrode without a diaphragm (TZ 1752), suitable reagent for generator electrodes without a diaphragm must be used.
A suitable catholyte must be filled into generator electrodes with a diaphragm (TZ 1753). The ideal filling quantity is approx. 4 ml. The level of the catholyte should be higher than that of the anolyte.

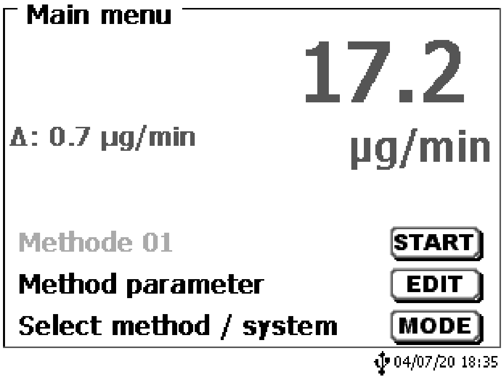
Stirring must be sufficiently. Stirring should result in a clear cone in the liquid without drawing many air bubbles into the liquid.



If there are problems with the coulometric KF titration, a water standard (a standard with a concentration of 1 mg / g is recommended) should be titrated first to exclude that only the sample matrix leads to problems.

Drift too high, start drift is not reached

Problem: After a titration, the drift no longer reaches the start drift (usually 10 µg / min), it remains permanently too high. The basic drift is the water that gets into the titration cell and is "titrated away".



Main menu

17.2

Δ: 0.7 µg/min

µg/min

Methode 01 START

Method parameter EDIT

Select method / system MODE

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There are various reasons for a too high drift - often it is a used desiccant, a leaky titration cell, side reactions or even just a used reagent.

Used desiccant

A common reason for a high drift is used desiccant. As a result, moisture from the air enters the titration cell and the drift increases. If the drift is high, the desiccant should first be replaced and the cell checked for leaks.

Untight titration cell

If the titration cell is not properly sealed, moisture from the air enters the titration cell and the drift increases. The septum through which the samples are injected is often worn out and must be replaced. At the latest when there are visible holes in the septum, it must be changed.

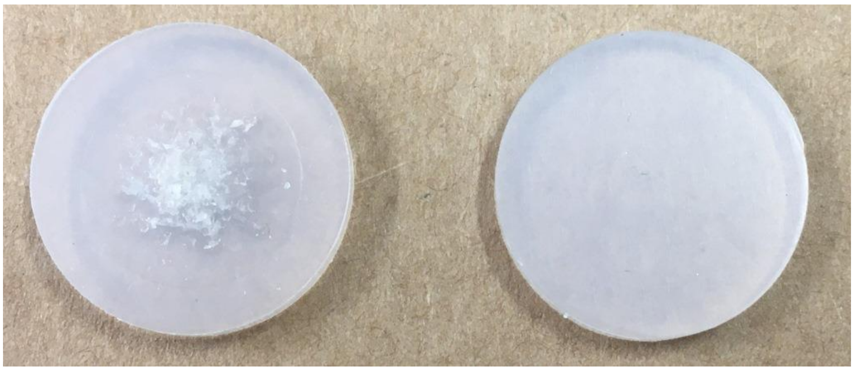


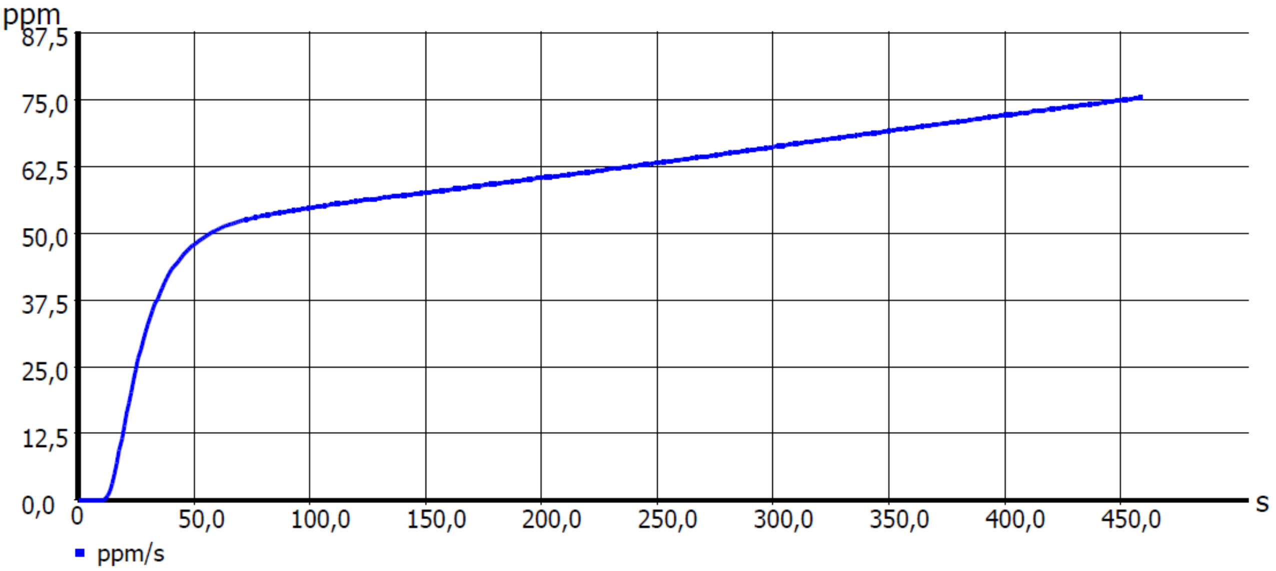
Fig.: The worn septum (left) must be replaced.

Less common is the leak at the ground joints of the titration cell. The ground joints should be cleaned and, if necessary, slightly greased. Only high quality silicone grease should be used and the grease should only be applied sparingly (!) in the upper third of the ground joints.

When using a pump to change the reagent, always some moisture gets into the titration cell through the tubes. As a result, the basic drift is always somewhat higher. It is better to remove the tubing after changing the reagent and plug the opening with a stopper.

Side reaktions

Side reactions are reactions of sample components with the KF reagent. Side reactions pretend a too high water content due to the consumption of iodine.



Side reactions cause e.g. Aldehydes and ketones, but also some additives, such as those used in motor oils. Some side reactions can be suppressed using suitable reagents, e.g. Aldehydes and ketones can be titrated using special reagents. For other side reactions, e.g. of oil additives or strongly basic oxides, this is not possible. The water content of such substances can only be determined by heating out the water in a KF oven and transferring it to the titration cell.

If there is a sample showing the side reactions in the titration cell, then only waiting for the end of the side reaction (reaching the start drift) or better a reagent change help.

Drift does not raise after sample addition

In a well-functioning titration cell, the drift increases after adding a few mg of water to well over 1000 µg / min. In good conditions, the generator electrode without a diaphragm can also reach up to 1500µg / min.

With special reagents, e.g. for aldehydes and ketones, the drift can remain below 1000µg / min.

Samples with a very low water content cause also a lower drift.

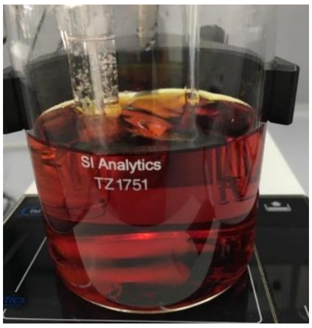
If the drift does not increase significantly as usual after sample addition, this can have several reasons.

The most common reasons are a used reagent or a used catholyte, sometimes a defective generator or indicator electrode

Remedy: Change reagent, fill up or change catholyte if necessary. Check electrodes.

Titrator titrates over

If the titrator titrates over, the reagent is colored dark brown due to the excess iodine. The dark brown color disappears after adding a little water.



The most common reasons are a used or unsuitable reagent, or a defective or dirty indicator electrode.

Remedy: Check the indicator electrode, clean if necessary (also the contacts of the 4mm connector).

Titration stops after input of sample weight

The titrator stops the titration immediately after adding the sample and entering the weight with a result of 0 µg, although the sample contains water. After that, the drift is often still very high.

If this effect occurs, this is usually due to the minimum titration time is too short.

The minimum time runs from the start of the titration. If the sample is not added within the minimum time, the end conditions are met at the end of the minimum time, the titration is ended.

The titrator just waits for the sample weight to be entered, then the calculations are carried out.

Remedy: Add the sample within the minimum time, increase the minimum time if necessary.

Clean and check electrodes

The tests described here should only be performed with fresh reagents.

Generator electrode TZ 1752 / TZ 1753

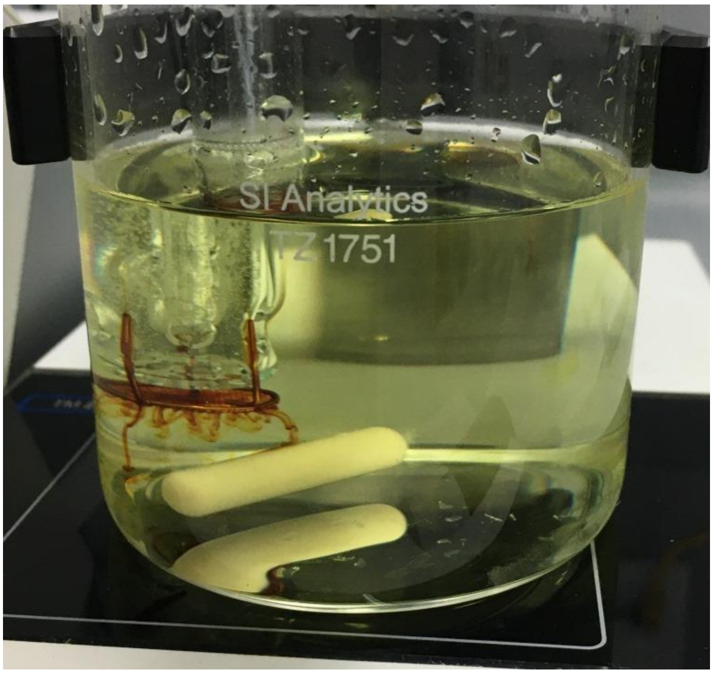
The generator electrode produces iodine at the anode (the lower platinum sieve), and hydrogen forms at the cathode (a platinum plate on the underside of the inner glass tube).
The platinum wires of the anode must not be subjected to mechanical loads. By bending these wires, the passage of the wires through the glass body can become leaky - penetrating reagent leads to the destruction of the electrode.

Visual inspection:

- No dirt / deposits, platinum parts silvery shiny.
- No brown liquid in the inner glass tube.
- glass parts not damaged.
- Connector clean, not corroded.

Cleaning:
The generator and indicator electrodes are made of glass and platinum and are therefore very chemically stable. However, the platinum parts should not be mechanically stressed, as this can lead to leakage through the glass.
In principle, everything can be used for cleaning that does not attack these materials. In the case of soiling that cannot be removed with water, ethanol, isopropanol or acetone also alkaline cleaning agents, conc. nitric acid or chrome sulfuric acid can be used. To clean the diaphragm, the electrode should be in the cleaning solution for a few hours. After cleaning the electrode is rinsed with dist. Water and then several times with methanol or ethanol. The electrode can be dried at a slightly elevated temperature (max. 80 ° C).
Isopropanol or acetone can be used to clean the 4mm banana plugs of the connection cable. The contact spring should be moved slightly during cleaning.

Functional test:
A ready-to use titration cell with fresh reagent is required for the functional test.
The stirrer is switched off and the cable of the indicator electrode is separated from the titrator. Now brown clouds (iodine) should form on the anode and gas bubbles should rise on the cathode inside the electrode:



If only a few gas bubbles form and no brown clouds, the generator electrode or the electrode cable is defective and must be replaced.

Indikator electrode KF 1150

Visual inspection:

- No dirt / deposits, platinum parts silvery shiny.
- No brown liquid in the glass tube.
- Glass parts not damaged.
- Platinum pins not bent together.
- Connector clean, not corroded.

If the two platinum pins of the electrode are bent together, they can be carefully (!) bent apart.

Cleaning:
In principle, everything can be used for cleaning that does not attack glass and platinum.
In the case of soiling that cannot be removed with water, ethanol, isopropanol or acetone also alkaline cleaning agents, conc. nitric acid or chrome sulfuric acid can be used. After cleaning the electrode is rinsed with dist. Water and then several times with methanol or ethanol. The electrode can be dried at a slightly elevated temperature (max. 80 ° C).

Isopropanol or acetone can be used to clean the 4mm banana plugs of the connection cable. The contact spring should be moved slightly during cleaning.

Functional test:
A ready-to use titration cell with fresh reagent is required for the functional test.
The indicator electrode is removed from the titration cell. If the drift now increases significantly, the indicator electrode is OK.
If the drift does not increase, the cable of the indicator electrode is separated from the titrator. The drift should now increase. In this case the electrode has a short circuit; usually the two platinum pins are bent together.
If there is no ready-to-use titration cell available or it is unclear whether the generator electrode is working, the indicator electrode can also be checked as follows:
The connectors for the generator electrode on the titrator are short-circuited. A cable with 4mm banana plugs on both sides is suitable for this, or, if not available, a piece of wire. The indicator electrode is separated from the titrator. The drift now increases to approx. 1500 µg / min.
The indicator electrode is connected to the titrator. The drift should remain at around 1500 µg / min.
If the drift drops to approx. 0 µg / min, the electrode has a short circuit. Usually only the two platinum pins are bent together (e.g. by a jumping stir bar). The platinum pins can be carefully (!) bent apart.

If the drift remains at approx. 1500 µg / min, the two platinum pins are carefully short-circuited with a piece of wire. The drift should now slowly drop to approx. 0 µg / min with an working indicator electrode.

If the drift remains at approx. 1500 µg / min with the short-circuited indicator electrode, the connector plugs of the electrode are cleaned with acetone or isopropanol. If this does not improve, the electrode is defective and must be replaced.

Any questions? Please contact the application team:

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