Metrohm

Application Bulletin 421

Automated coulometric Karl Fischer titration

Branch

General analytical chemistry, private laboratories; organic chemistry, chemistry pharmaceutical industry; petro chemistry, biofuels; energy, power plants

Keywords

Titration; Karl Fischer titration; coulometric; automation; MATi 4; water content; branch 1; branch 3; branch 4; branch 5; branch 16

Summary

This Application Bulletin provides information on the MATi 4 system (MATi = **M**etrohm **A**utomated **Ti**tration). MATi 4 is a completely configured system used for the automated coulometric Karl Fischer titration and the water content determination in liquid samples. The maximum sample volume is 5 mL. Up to 160 samples are filled into vials and covered with the crimp cap. In this way the samples do not loose or absorb any water. The samples are aspirated and injected via a needle into the coulometric cell. The system is controlled by the ***tiamo***™ software.

Instrument and accessories

The MATi 4 system consists of:

- Sample Changer
- Titrator with KFC mode
- Coulometric titration vessel including electrodes
- 10 mL buret for sample handling
- Magnetic Stirrer
- Required accessories for the KF titration
- 6 mL crimp vials

Electrodes

Double Pt-wire electrode	6.0341.100
Generator electrode with diaphragm	6.0344.100
Generator electrode without diaphragm	6.0345.100

Reagents

Standard reagents for coulometric water determination can be used:

- Anolyte for the coulometric cell (depending on the sample)
- Catholyte for the generator electrode with diaphragm

Standard

Commercially available water standards with water contents between 0.1 and 5 mg/g should be used to check the system.

System preparation

Position of the needle

For pressure equalization a double hollow needle must be used (figure 1).

When adjusting the working position in the sample vial it must be ensured that the middle hole of the needle is not immersed in the sample as this could lead to carry-over. However, the middle hole must be in the vial in order to ensure the pressure equilibrium.

Figure 1: double hollow needle with venting holes

For the aspiration of the air bubbles (see method description on page 2), the needle should be in the vial, but without being immersed in the sample. If this position is not possible, the complete needle should be outside the vial.

Sample preparation

The samples are filled into the vials and closed with the crimp cap. All vials should be filled up to the vial shoulder (see figure 2).

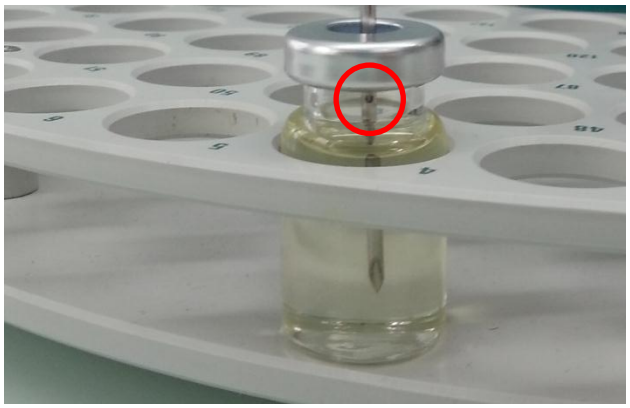


Figure 2: Sample vial filled up to the shoulder with immersed needle. The middle hole (red circle) is not immersed in the sample.

Coulometric cell

The level of the KF reagent should be at approx. 175 mL to have enough reagent for the preparation step and rinsing of the sample loop. It is important that during the rinsing steps and for the tubing preparation at the beginning of each sample measurement, reagent and not air is aspirated into the loop.

The swing head configuration should be changed slightly from the recommended setting. The “max. swing range” should be limited to 105.0° instead of 117.0° to prevent the needle from bumping into the generator electrode.

The needle should not be in the middle of the stirring funnel, otherwise air is aspirated into the tubing which diminishes the accuracy and repeatability of the pipetting and of the end results.

Pipetting tube

The short end of the pipetting tube is connected to the needle and the other end is connected to the Dosino. Prior to every series the pipetting tube needs to be completely filled with conditioned reagent.

A low aspiration and dosing rate should be chosen in order to pipet the solutions as precisely as possible. For MATi 4, an aspiration rate of 2.5 mL/min and a dosing rate of 5 mL/min are recommended.

If higher rates are used a liquid film can form on the wall of the tube due to friction; this leads to wrong pipetting or dosing volumes and therefore irreproducible results.

The pipetting tube has a volume of 10 mL. Therefore the maximum volume which can be aspirated is 10 mL, which corresponds to sample volume plus rinsing volume.

Constant reagent level

Depending on the sample size and the rinsing volume, the liquid level in the coulometric vessel can either increase or decrease. It is important that the reagent is kept at a stable level.

If the level is too low, air is aspirated instead of conditioned reagent. To aspirate and dose accurate sample volumes it is essential that the pipetting tube is filled air bubble free.

In case the level is too high, the middle hole of the needle is immersed in the reagent. This can lead to a blocking of the needle ventilation and to contamination of the sample with humid KF reagent.

An aspiration tube is therefore connected to the coulometric cell and a Dosino to regularly remove an excess volume or add fresh reagent (see figure 3). The aspiration tip is positioned in a way that the reagent level is at approx. 175 mL after aspiration. In case the aspiration tube is too long, it can be shortened to the optimal length.

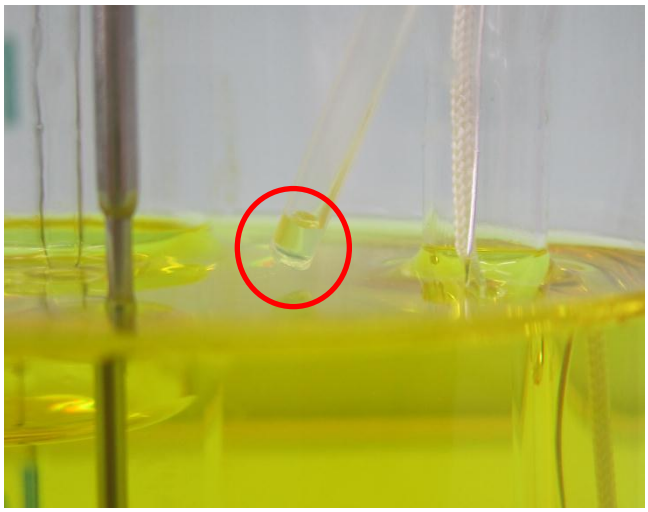


Figure 3: Aspiration tube for removing excess of reagent.

Method description

The sample is sealed hermetically with a septum before being placed on the rack. By means of the double hollow needle and a pipetting tube the sample is pipetted into the closed conditioned titration cell:

- The swing head moves to the cell
- The needle is lowered to the work position
- The tubing is filled with conditioned KF reagent
- The needle is slightly lifted out of the KF reagent
- An air bubble is created
- The needle is lowered to the work position
- A defined amount of KF reagent is aspirated into the tubing as rinsing solution
- The needle is slightly lifted out of the KF reagent
- An air bubble is created
- The needle is lifted to the shift position
- The Swing Head moves to the sample

- The needle is lowered to the work position
- The sample is aspirated
- The needle is slightly lifted out of the sample
- An air bubble is created
- The needle is lifted to the shift position
- The Swing Head moves to the external position
- The needle pierces the septum and the sample is dosed into the conditioned titration cell where the water determination takes place.

Remark: The air bubbles serve as a barrier between the different pipetting solutions and are avoiding a mixing. However, they should be small enough (100 to 200 µL) to ensure a high accuracy of the pipetting steps.

Calculation

$$\text{water content (ppm)} = \frac{EP_{sample}}{V_{sample} \times \rho}$$

EP_{sample}: Determined amount of water at the end of titration [µg]

V_{sample}: Sample volume [mL]

ρ: Density of the sample [g/mL]

Remark: The density of the sample must be known.

Comments

- The sample size should be 5 mL or smaller.
- Close the crimp vials immediately after the filling to avoid changes of the water content.
- For measurements of samples with low water content, dry the vials in a desiccator for at least 2 hours.
- For the correct calculation of the sample weight the density of the sample needs to be known.
- A low aspiration rate should be chosen in order to pipet the solutions as precisely as possible.
- The stirring speed should be high enough to ensure a proper mixing.
- A picture of the complete MATi 4 system can be found in the appendix.
- The rack is not resistant against certain organic substances (e.g. anisole). Some KF reagents contain ingredients which can damage the rack.
- For best results, fresh reagents should be used.
- It is essential that the level of the reagent in the titration cell remains more or less on the same level.
- The tip of the needle should be immersed in the reagent to avoid aspiration of air instead of reagent.
- The middle hole should neither be immersed in the reagent nor in the sample. This would lead to cross contamination of the samples.
- The water from the KF water standards (especially the 1.0 and 0.1 mg/g standards) tends to evaporate from the liquid into the headspace of the vial, which leads to too low results. For this reason, it is recommended to fill the vials completely with standards. For the same reason, only one pipetting per vial should be performed.

Literature

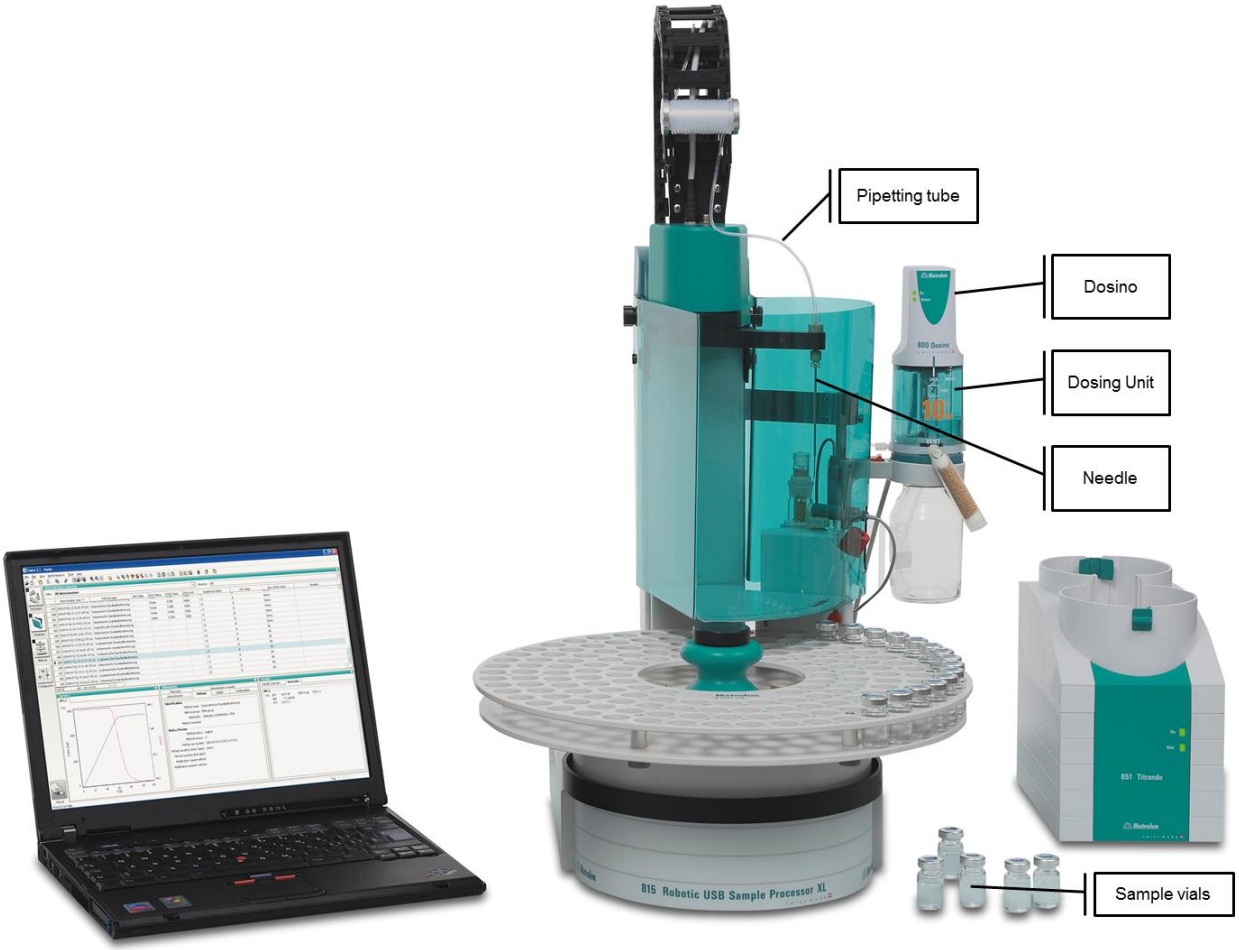
- Monograph: Water Determination by Karl Fischer Titration

Author

Competence Center Titration

Metrohm International Headquarters

Appendix


Pipetting tube
Dosino
Dosing Unit
Needle
Sample vials
815 Robotic USB Sample Processor XL
851 Titrando