Coulometric Karl Fischer titration: diaphragm-free cell, cell design and applications

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Outline

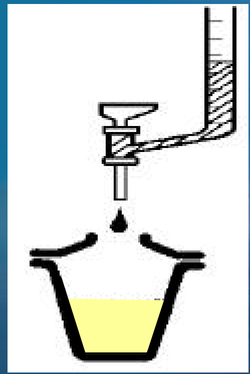
- Coulometric Karl Fischer titration
- Diaphragm-free cell
- Applications, Instrumentation, Examples

Volumetric and coulometric Karl Fischer titration for water determination

The Karl Fischer reaction: Iodine reacts stoichiometrically with water

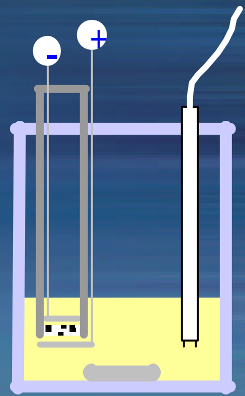
$ROH + SO_2 + B \rightarrow (BH)SO_3R$

$(BH)SO_3R + 2B + I_2 + H_2O \rightarrow (BH)SO_4R + 2BHI$



Volumetric Karl Fischer Titration:
Iodine is added with burette during titration.

Water as a major component: 100 ppm - 100 %

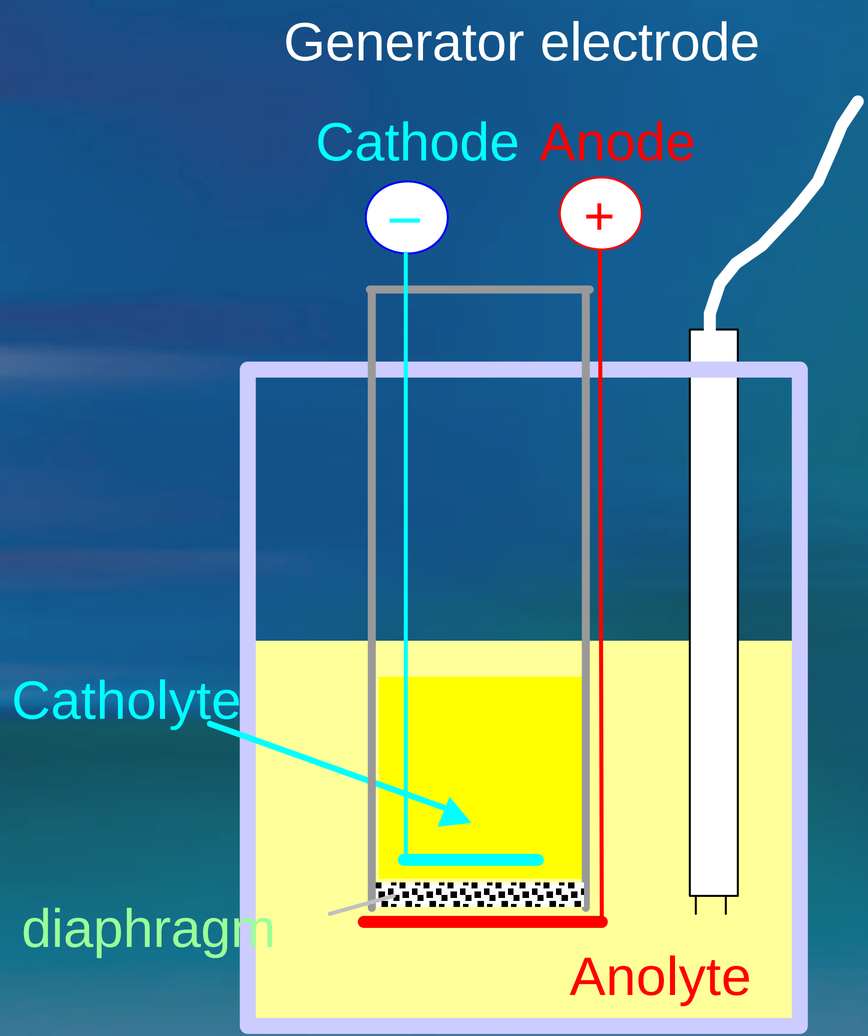


Coulometric Karl Fischer Titration:
Iodine is generated electrochemically during titration

$2\,I^- \rightarrow I_2 + 2\,e^-$

Water in trace amounts: 1 ppm - 5 %

Coulometric Karl Fischer titration cell



Indicator electrode:
Double platinum pin electrode

Anolyte:
Sulfur dioxide, Imidazole, Iodide, various solvents for various applications:
Methanol or Ethanol with Chloroform, Octanol, Ethylene glycol

Catholyte:

Same or modified solution

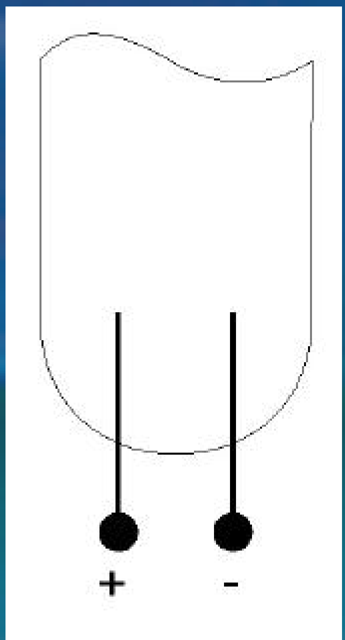
Control of the Karl Fischer titration: indication

METTLER TOLEDO DL32/DL39:

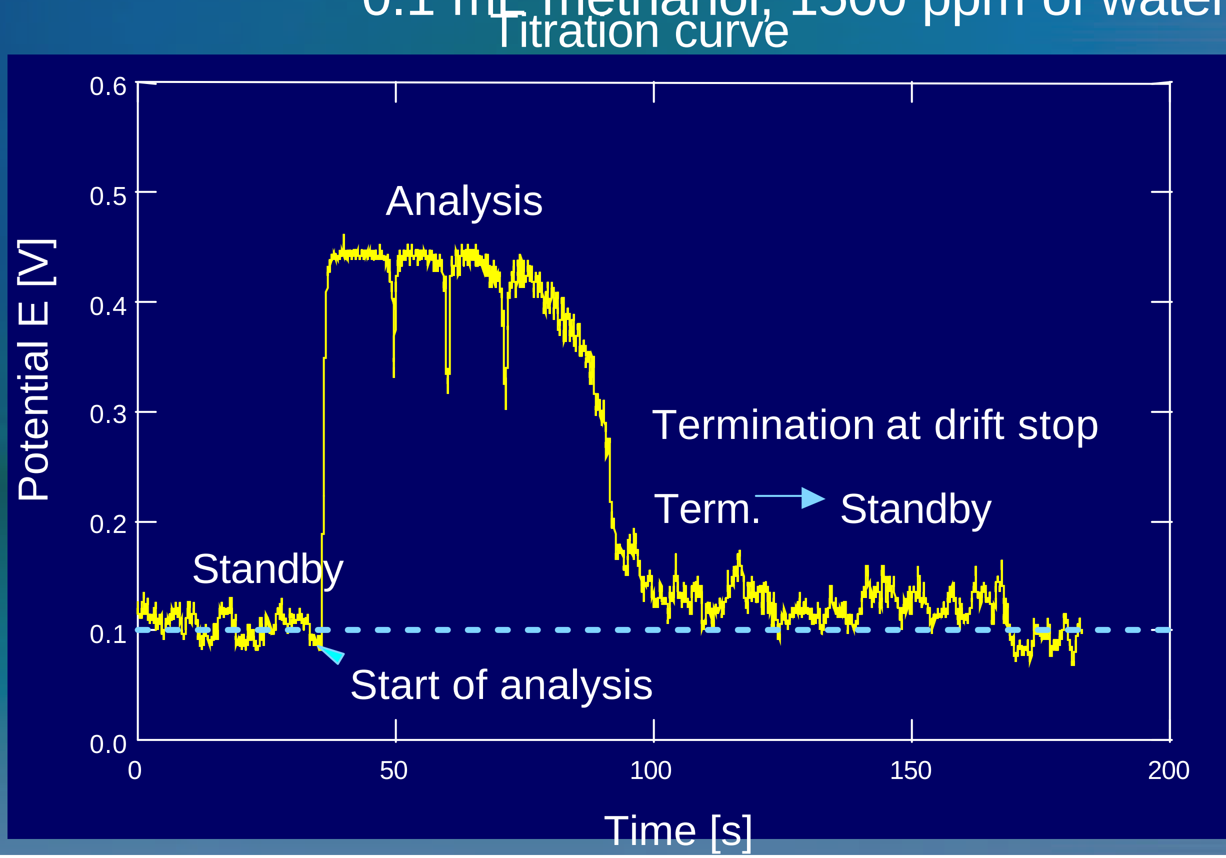
DC polarization at double platinum pin electrode (two-electrode potentiometry)

Polarization current: 1, 2 or 5 uA

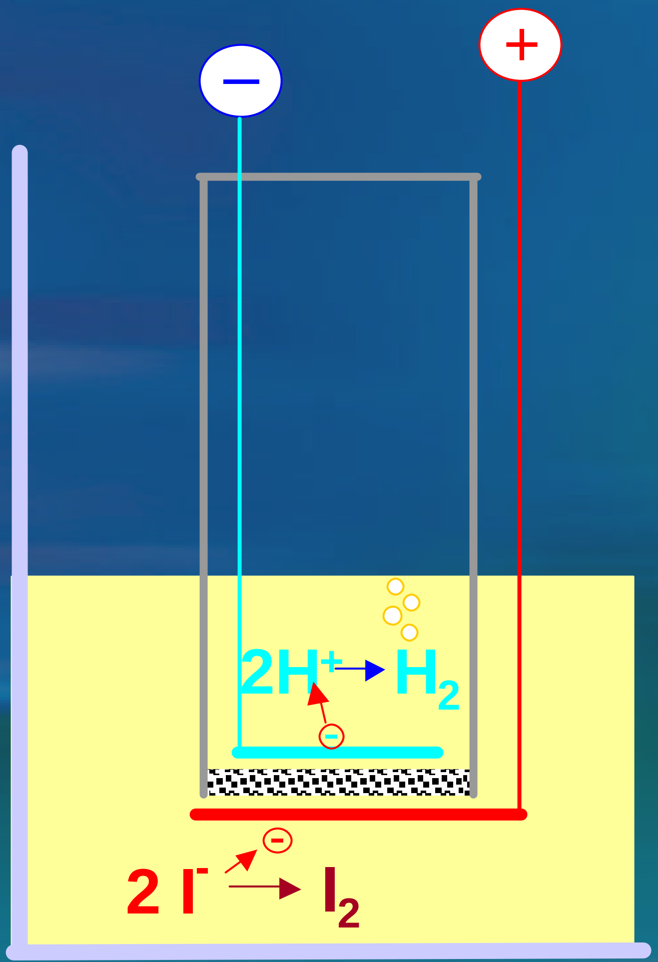
Sample: 0.1 mL methanol, 1500 ppm of water



$$i_a^+ = i_c^-$$



Coulometric Karl Fischer titration: iodine generation



Anodic reaction:

Iodine production by oxidation of iodide

$2\ I^- \rightarrow I_2 + 2\ e^-$

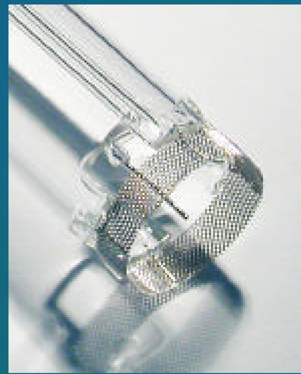
Cathodic reaction:

Hydrogen production through reduction of H^+ ions

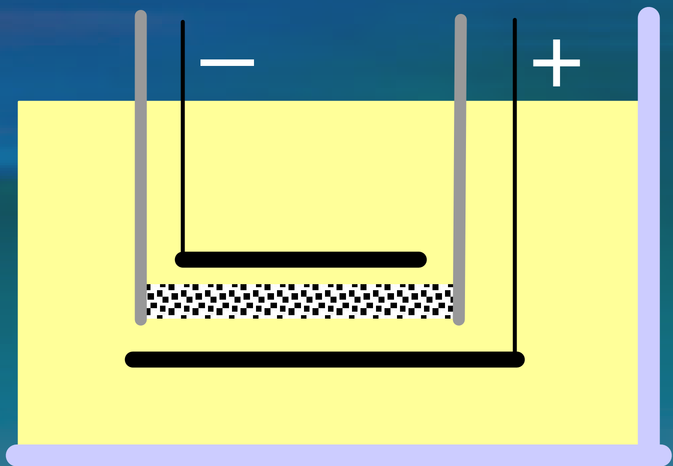
$2\ [RN]H^+ + 2\ e^- \rightarrow H_2 + 2RN$

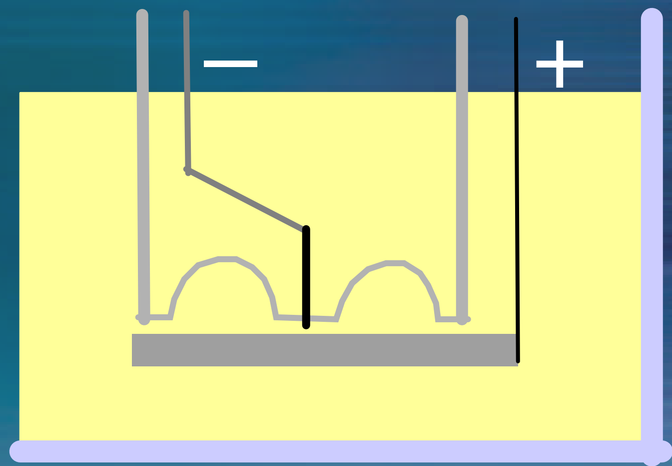
Coulometric Karl Fischer titration:
cell with diaphragm and diaphragm-free cell

Current
generator
„electrode“ for
cell with
diaphragm



Current
generator
„electrode
“ for
diaphrag
m-free cell





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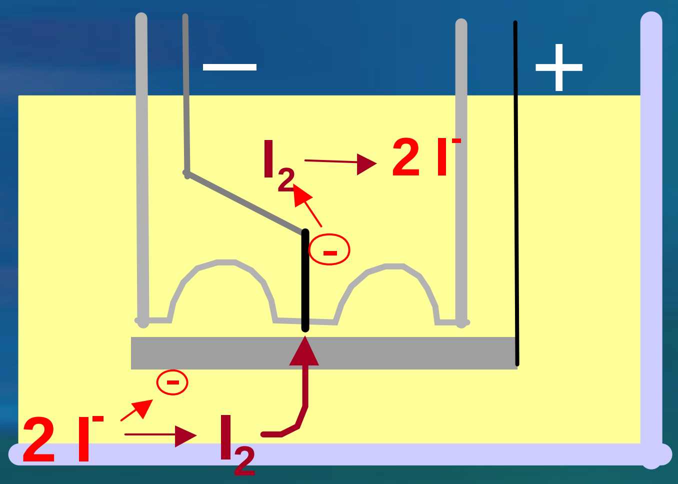
Coulometric Karl Fischer titration: cell without diaphragm

Efficiency loss at non-optimized diaphragm-free coulometric KF titration



Problem:

Efficiency loss through chemical or electrochemical iodine reduction with oxidizable reduction products or at the counter-cathode

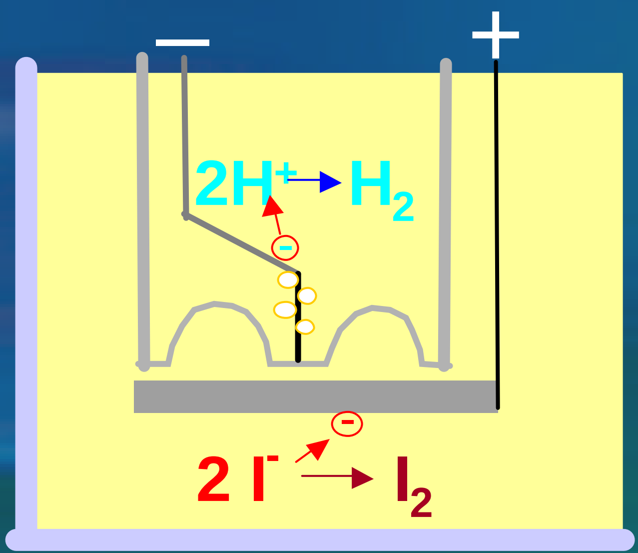
→ too high water recovery

→ Engineering of an optimized diaphragm-free current generator is rec

Coulometric Karl Fischer titration: cell without diaphragm

Optimization of the diaphragm-free coulometric KF titration:

Geometry optimization



- Anode:
  homogeneous current distribution
- Cathode:
  small cathode surface area → protection through hydrogen bubbling
- Sufficient stirring
- Geometrical separation of the electrodes

Coulometric Karl Fischer titration: cell without diaphragm

Optimization of the diaphragm-free coulometric KF titration: Electrochemical current generation

• Generated current pulses of 400 mA, 200 mA, 100 mA, 60 mA are feasible. Large pulses are favourable, since the production of oxidizable reduction products is diminished.

• Voltage at the generator cell must be high enough for low-conducting electrolytes.
Example: 28 V available at DL32/DL39 for current generation, which is sufficient for low-conducting electrolytes to approx. 5 mS/cm.

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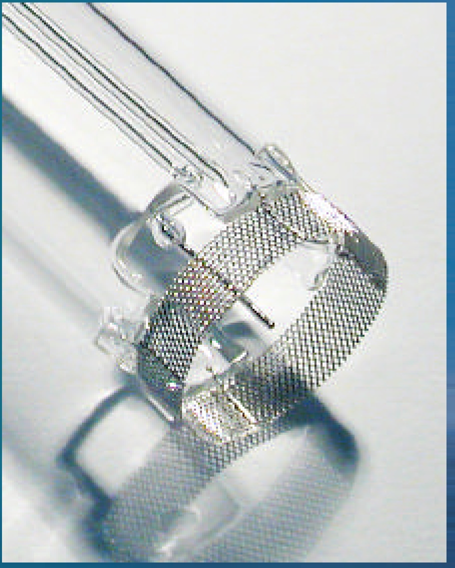
Coulometric Karl Fischer titration: cell without diaphragm

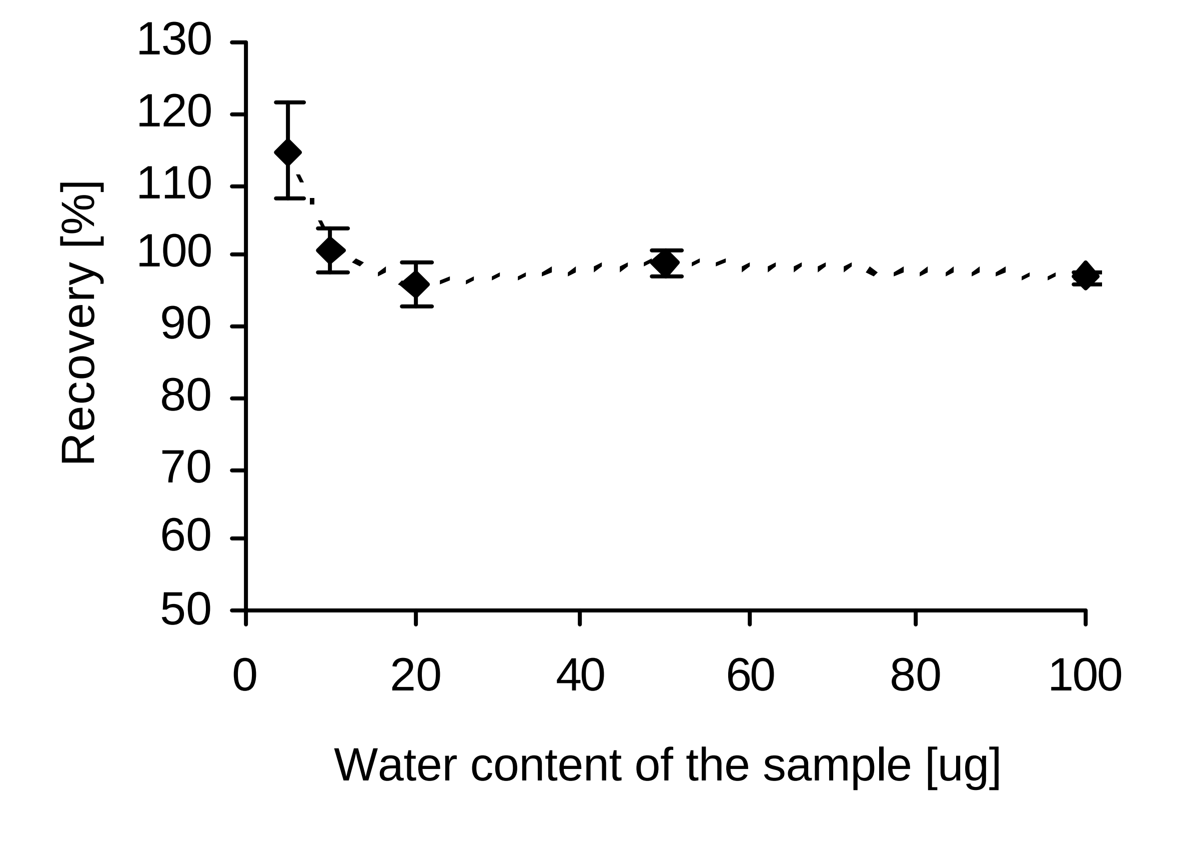
Advantages of diaphragm-free KF coulometry: Simple ease-of-use

- Titration cell is easier to clean and refill
- No clogged-up diaphragm
- No contaminants from diaphragm
- Lower drift



- Optimized diaphragm-free coulometric KF titration allows precise trace water determinations down to less than 10–20 ug of water.

Coulometric Karl Fischer titration: cell without diaphragm



Recoveries with diaphragm-free KF titration with a METTLER TOLEDO DL39 coulometer for a HYDRANAL 100 ppm standard solution
(electrolyte: HYDRANAL Coulomat AG/CG)

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Applications: Coulometry of soluble samples

- Samples that are easily soluble:

  Solvents (alcohols, ethers, esters, hydrocarbons, halogenated hydrocarbons, nitro-compounds, etc.)

  Use standard electrolytes for cell with/without diaphragm, e.g. Riedel-de Haën HYDRANAL, Merck APURA, and J.T. Baker HYDRA-POINT

- Samples that do not easily dissolve:

  Edible oils, etheric oils, ointments, etc.

  Add hexanol, octanol or decanol to the electrolyte, or use special electrolytes, e.g. HYDRANAL Coulomat AG-H

- Mineral oils, transformator oils, silicon oils, etc.

  → Add chloroform to the electrolyte, or use special electrolytes, e.g. HYDRANAL Coulomat Oil

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Applications: Coulometry of soluble samples

Ketones and aldehydes:
they react with methanol, producing H_2O as a by-product.

Special KF reagents for ketones are required, e.g. HYDRANAL Coulomat AK/(CG-K) [cell with/without diaphragm]

Note:
Short aldehydes (e.g. acetaldehyde) are oxidized at the anode, with H_2O as a by-product.
Long-chain and aromatic aldehydes are no problem.

Applications: Special samples

Special samples:

Hardly-soluble or non-soluble samples

Samples that undergo side-reactions with the Karl Fischer electrolyte

Non-soluble samples that release water only at elevated temperatures

Samples with high viscosity

→ Extraction of water by external extraction

→ Extraction of water with an oven, with transfer of the carrier gas to the Karl Fischer cell

DO307 oven

Stromboli sample changer oven

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Instrumentation:
DO307 and Stromboli Sample changer oven

DL39 - DO307

DL39 - Stromboli

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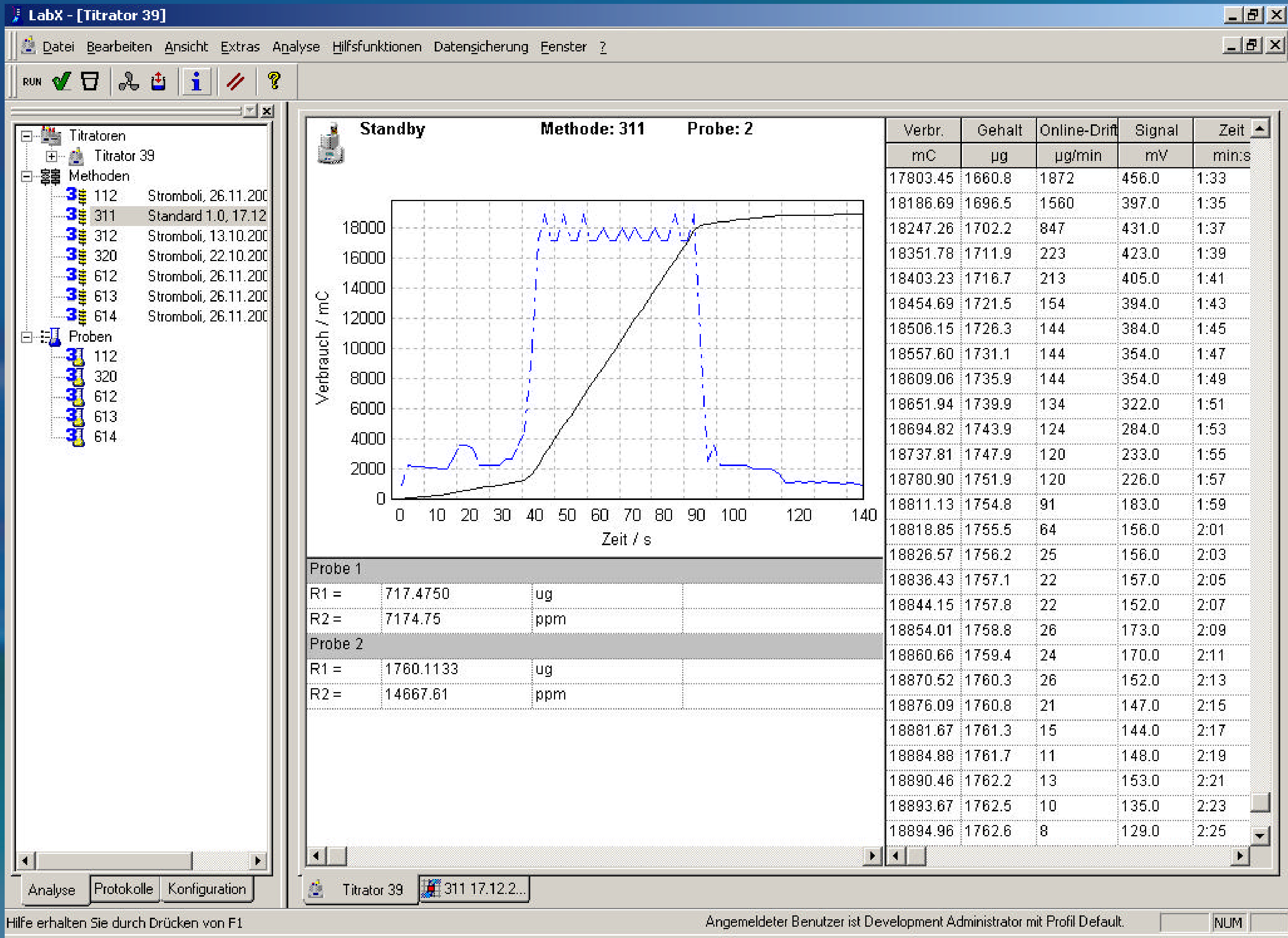
Instrumentation: LabX titration software



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Foodstuffs: Sample addition

Solid samples: external extraction/dissolution, drying oven

Liquid samples: direct injection

Sample	Method	KF-Reagents	Water content
Sucrose Surface water	External extraction in chloroform (15 min at 25°C)	Coulomat AG/ Coulomat CG	71.5 ppm
Sucrose Total water	External dissolution in formamide (15 min at 50°C)	Coulomat AG/ Coulomat CG	533.7 ppm
Olive oil	Direct injection with syringe	Coulomat AG with 40 vol.% decanol/ Coulomat CG	836 ppm
Rape oil	Direct injection with syringe	Coulomat AG with 40 vol.% decanol/ Coulomat CG	424 ppm
Cooking salt	Heating with DO307 oven, 300°C	Coulomat AG Oven/ Coulomat CG	359.6 ppm
Cinnamon powder	Heating with Stromboli oven, 180°C	Coulomat AG Oven/ Coulomat CG	4.8%
Garlic powder	Heating with Stromboli oven, 180°C	Coulomat AG Oven/ Coulomat CG	10.1%

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Foodstuffs: Edible oils

Sample	Sample amount	Method	KF reagents	Water content, cell with diaphragm	Water content, cell without diaphragm
Olive oil	0.1–0.3 g	Direct injection with syringe	With diaphragm: Hydranal Coulomat AG-H/CG Without diaphragm: Hydranal Coulomat AD + 20% Octanol	507 ± 7 ppm	504 ± 13 ppm
Corn seed oil	0.1–0.3 g	Direct injection with syringe	With diaphragm: Hydranal Coulomat AG-H/CG Without diaphragm: Hydranal Coulomat AD + 20% Octanol	378 ± 4 ppm	376 ± 6 ppm
Sunflower oil	0.1–0.3 g	Direct injection with syringe	With diaphragm: Hydranal Coulomat AG-H/CG Without diaphragm: Hydranal Coulomat AD + 20% Octanol	698 ± 22 ppm	657 ± 2 ppm

Sunflower oil: Difference in water content may be due to slower dissolution leading to turbidity of electrolyte after a few sample injections. Turbidity disappears after long stirring.

Foodstuffs: Spices, teas

Sample	Sample amount	Method	KF reagents	Water content, cell with diaphragm	Water content, cell without diaphragm
Marjoram spice	0.05 g	Heating with Stromboli oven, 180°C, 15 min.	Baker Hydra-Point Coulometric Oven	8.58 ± 0.17 %	8.9 ± 0.2 %
Marjoram spice	5 g	External extraction with methanol	Coulomat AG/CG Coulomat AG	8.33 ± 0.14 %	8.33 ± 0.15 %
Black tea	0.05 g	Heating with Stromboli oven, 180°C, 15 min.	Baker Hydra-Point Coulometric Oven	6.35 ± 0.18 %	6.3 ± 0.2 %
Black tea	2 g	External extraction with methanol	Coulomat AG/CG Coulomat AG	6.10 ± 0.16 %	6.10 ± 0.15 %

Difference in water recoveries may be due to sample preparation procedure. Optimisation of the sample preparation procedure is needed for each sample type.

Conclusions

Coulometric Karl Fischer titration is well suited for water determination in foods with low water content.

A diaphragm-free coulometric Karl Fischer titration cell is easy to use (easy cleaning and refilling, no clogging of the diaphragm), shows a lower drift and may replace a cell with diaphragm in most cases.

Diaphragm-free Karl Fischer coulometry has been optimized even for very low water content determinations and allows precise water determinations down to less than 10–20 µg of water.

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