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

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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 %

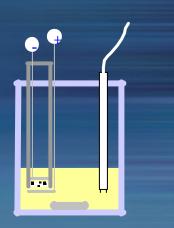


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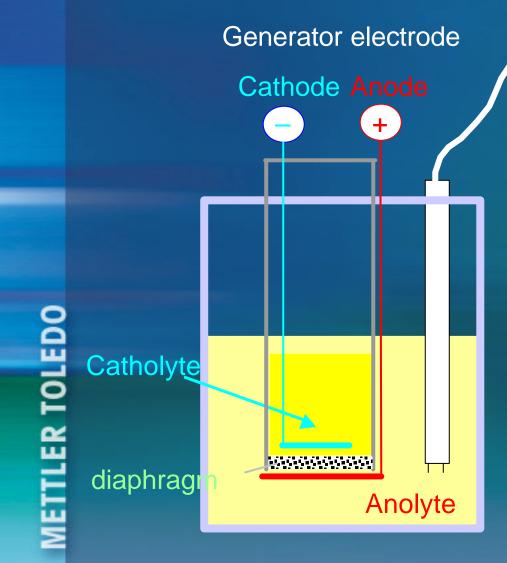
Coulometric Karl Fischer Titration: lodine is generated electrochemically during titration

 $2 \downarrow^{-} \rightarrow \downarrow_{2} + 2 e^{-}$

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

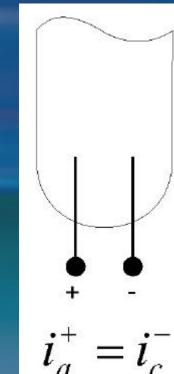
METTLER TOLEDO DL32/DL39:

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

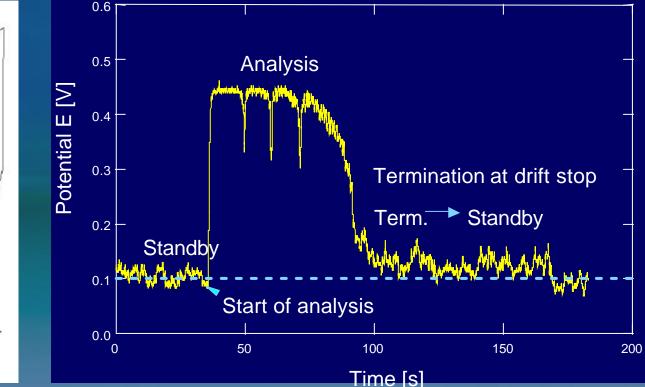
Polarization current: Sample:

1, 2 or 5 uA

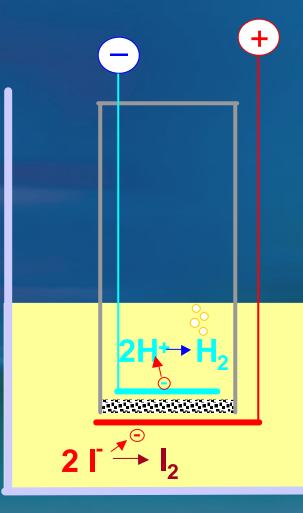
0.1 mL methanol, 1500 ppm of water Titration curve



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Coulometric Karl Fischer titration: iodine generation



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Anodic reaction: Iodine production by oxidation of iodide

 $2 I^{-} \rightarrow I_{2} + 2 e^{-}$

Cathodic reaction: Hydrogen production through reduction of H⁺ ions

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

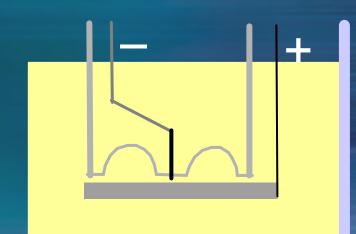
Coulometric Karl Fischer titration: cell with diaphragm and diaphragm-free cell

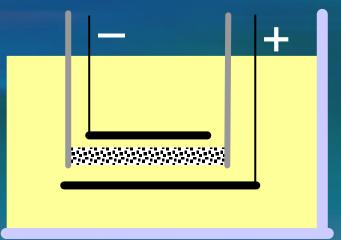


Current generator "electrode" for cell with diaphragm



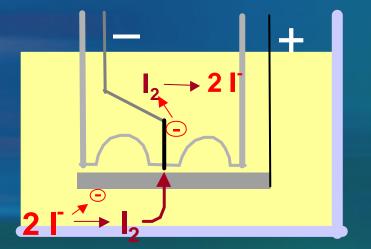
Current generator "electrode " for diaphrag m-free cell





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

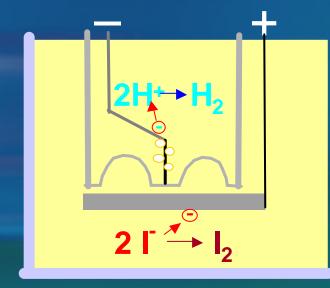


Problem:

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

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

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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.

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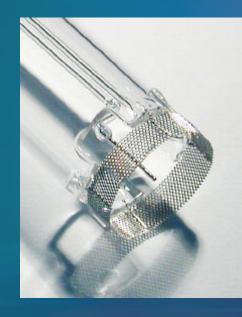
 Voltage at the generator cell must be high enough for lowconducting electrolytes.
Example: 28 V available at DL32/DL39 for current generation, which is sufficient for low-conducting electrolytes to approx. 5 mS/cm.

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

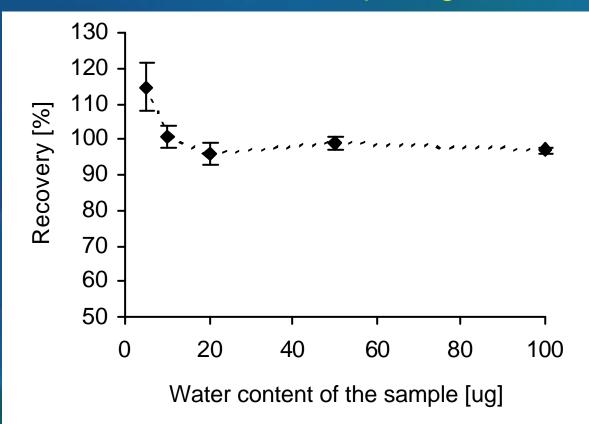
- Titration cell is easier to clean and refill
- No clogged-up diaphragm
- No contaminants from diaphragm
- Lower drift

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• Optimized diaphragmfree coulometric KF titration allows precise trace water determinations down to less than 10–20 ug of water.



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

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

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.

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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

 \rightarrow Extraction of water by external extraction

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→ Extraction of water with an oven, with transfer of the carrier gas to the Karl Fischer cell DO307 oven Stromboli sample changer oven

Instrumentation: DO307 and Stromboli Sample changer oven

DL39 - DO307

DL39 - Stromboli



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Instrumentation: LabX titration software

LabX - [Titrator 39]

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Foodstuffs: Sample addition

Solid samples: external extraction/dissolution, drying oven Liquid samples: direct injection

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

Foodstuffs: Edible oils

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

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Sunflower oil:Difference in water content may be due to slowerdissolutionleading to turbidity of electrolyte after afew sample injections.Turbidity disappears after long stirring.

Foodstuffs: Spices, teas

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

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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.