Titration Application Note

Coulometric Karl Fischer Titration

Comparison of Water Standards

Karl Fischer (KF) Titration is the method of choice for the determining of the water content in a vast variety of samples such as pharmaceuticals, petrochemical products, plastics, foods, and beverages. Compared to other analytical methods, KF titration is a simple, quick and unexpensive technique to selectively determine the water amount present in a sample.

Appropriate instrument qualification, calibration and maintenance procedures ensure correct measurement results. The qualification procedure of the titration instrument guarantees customers the accuracy, precision, and uptime in their daily workflow. In particular, the verification of the needed accuracy and precision of the KF titration using certified water standards is the a mandatory step to complete the instrument verification.

In this application, this step is performed for the coulometric KF titration using two commonly used water standards, i.e., the 1.0 mg/g and 0.1 mg/g liquid water standard. The water standards are titrated using different coulometric electrolytes for both generator cells, i.e., with and without diaphragm.

Figure 1: METTLER TOLEDO C30SD Compact KF Coulometer with diaphragmless generator cell.

METTLER TOLEDO

Introduction

The Karl Fischer titration takes place in a solution mainly consisting of an alcohol, sulfur dioxide, and an organic base. The exact reagent composition used for KF titration influences the speed and accuracy of the analysis. This leads to a continuous development of KF reagents, which helps to further improve the water content determination in terms of accuracy, stability, simplicity, safety, and environmental acceptability.

This application describes the water content determination in certified water standards used to verify the equipment performance. Different coulometric electrolytes are tested for the generator cell with and without diaphragm.

Sample Preparation and Procedures

1. Generator cell with diaphragm: First add 5 mL catholyte in the generator cell. Subsequently, 100 mL analyte is added in the titration cell.
2. Generator cell without diaphragm: only one electrolyte is needed, i.e., 100 mL anolyte.
3. After start, the pretitration is performed to remove residual water in the titration cell.
4. Sample determination: 1-1.5 g of 1 mg/g or 1.5-2.5 g liquid water standard is added to the cell, respectively.
5. Two methods were used: one with standard parameters (M904A) [1], and one (M904B) with optimized parameters for low water content of 100 ppm [2].

Chemistry

$CH_3OH + SO_2 + 3\ RN + I_2 + H_2O \rightarrow$
$(RNH)SO_4CH_3 + \ \ 2\ (RNH)I$

Analyte:
Water, H_2O, M = 18.02 g/mol, z = 1

Chemicals

Generator cell without diaphragm:
- Aquagent® Coulometric AG - Anolyte (Scharlau, nr. AQ00580500)

Generator cell with diaphragm:
- Aquagent® Coulometric A - Anolyte (Scharlau, nr. AQ00180500)
- Aquagent® Coulometric AG - Anolyte (Scharlau, nr. AQ00580500)
- Aquagent® Coulometric CG - Catholyte (Scharlau, nr. AQ00140050)

Water standards:
- HYDRANAL™ Water Standard 1.0 (34426)
- HYDRANAL™ Water Standard 0.1 (34847)

Instruments and Accessories

- KF Compact Coulometer C30S(X and D), or Titration Excellence T7/T9 with Coulometric KF Kit (D: 30267112 , X: 30267113)
- XPR205 Analytical balance (30355411)
- DM143-SC electrode (51107699)
- 10 mL syringe (00071482)
- LabX software

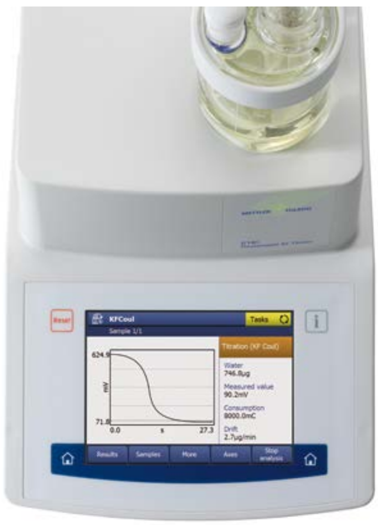

Figure 2: The displayed titration curve shows the measured potential value E (mV) during titration (s).

Results

1 mg/g water standard (Method M904A, standard parameters):

Generator cell without diaphragm	Electrolyte: Aquagent® Coulometric AG					
		Content mg/g	Recovery %	n	m g	TIME s
Water std 1 mg/g	average	0.999	99.206	6	1.2-1.6	108-112
1.007 ± 0.013 mg/g	s	0.002	0.166			
	srel (%)	0.167	0.167			
1.003 ± 0.012 mg/g	average	0.996	99.335	6	1.0-1.6	108-109
	s	0.003	0.326			
	srel (%)	0.328	0.328			

Generator cell with diaphragm	Anolyte: Aquagent® Coulometric A Catholyte: Aquagent® Coulometric CG					
		Content mg/g	Recovery %	n	m g	TIME s
Water std 1 mg/g	average	1.006	99.934	6	1.1-1.5	107-109
1.007 ± 0.013 mg/g	s	0.003	0.342			
	srel (%)	0.342	0.343			
1.007 ± 0.013 mg/g	average	0.993	98.626	6	1.0-1.6	107-108
	s	0.002	0.230			
	srel (%)	0.233	0.233			
1.007 ± 0.013 mg/g	average	1.006	99.901	6	1.0-1.6	107-110
	s	0.004	0.426			
	srel (%)	0.426	0.426			

Generator cell with diaphragm	Anolyte: Aquagent® Coulometric AG Catholyte: Aquagent® Coulometric CG					
		Content mg/g	Recovery %	n	m g	TIME s
Water std 1 mg/g	average	0.989	98.588	6	1.0-1.7	108-117
1.003 ± 0.012 mg/g	s	0.004	0.430			
	srel (%)	0.436	0.436			
1.003 ± 0.012 mg/g	average	0.987	98.405	6	1.0-2.0	108-111
	s	0.006	0.550			
	srel (%)	0.559	0.559			
1.003 ± 0.012 mg/g	average	0.990	98.654	6	1.0-2.0	108-148
Control Band = 400 mV	s	0.003	0.301			
	srel (%)	0.305	0.305			

0.1 mg/g water standard (Method M904B, optimized parameters for low water content):

Generator cell without diaphragm	Electrolyte: Aquagent® Coulometric AG					
		Content mg/g	Recovery %	n	m g	TIME s
Water std 0.1 mg/g	average	0.110	103.302	6	1.2 - 2.5	64-102
0.106 ± 0.008 mg/g	s	0.002	1.431			
	srel (%)	1.385	1.385			
0.106 ± 0.008 mg/g	average	0.109	102.988	6	1.0 - 2.3	61-94
	s	0.001	1.103			
	srel (%)	1.071	1.071			
0.106 ± 0.008 mg/g	average	0.113	106.918	6	1.2 - 1.7	53-70
	s	0.004	3.304			
	srel (%)	3.090	3.090			

Generator cell with diaphragm	Anolyte: Aquagent® Coulometric A Catholyte: Aquagent® Coulometric CG					
		Content mg/g	Recovery %	n	m g	TIME s
Water std 0.1 mg/g	average	0.100	101.010	6	1.4-1.7	49-59
0.099 ± 0.009 mg/g	s	0.001	0.825			
	srel (%)	0.816	0.816			
0.102 ± 0.009 mg/g	average	0.100	97.876	6	1.3-2.0	48-62
	s	0.001	0.964			
	srel (%)	0.985	0.985			
0.102 ± 0.009 mg/g	average	0.100	97.712	6	1.3-2.0	51-68
	s	0.001	0.800			
	srel (%)	0.819	0.819			

Generator cell with diaphragm	Anolyte: Aquagent® Coulometric AG Catholyte: Aquagent® Coulometric CG					
		Content mg/g	Recovery %	n	m g	TIME s
Water std 0.1 mg/g	average	0.099	100.168	6	1.0 - 1.6	52-59
0.099 ± 0.009 mg/g	s	0.001	0.760			
	srel (%)	0.759	0.759			
0.102 ± 0.009 mg/g	average	0.097	98.148	6	1.6-2.4	78-107
	s	0.001	1.487			
	srel (%)	1.515	1.515			

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Remarks

Titration

- The water content was determined using standard control parameters [1] and optimized parameters for low water content [2].
- The certified value of the standard is entered as auxiliary value "H" in the titrator setup.
- Wait until the online drift is below 5 µg/min to achieve correct results. In fact, a too high drift value is strongly affecting the results, especially for the 0.1 mg/g water standard.
- The accuracy and the repeatability are improved when using a large sample size.
- The parameter TIME refers to the duration of a sample analysis from the end of standby mode to the end of the titration method function. Thus, it also includes the waiting for sample addition, and the stir time before titration.

Accuracy

- The accuracy achieved can be easily be verified by calculating the recovery rate in %.
- For the 1 mg/g standard, i.e., 1000 ppm, excellent recovery rates have been determined for all reagents and generator cells used, with values varying from 98.4 % up to 99.9 %.
- For the 0.1 mg/g, i.e., 100 ppm, reasonable recovery rates have been achieved, with values between 97.9% and 106.9%. Since the water content is very low, a higher deviation from the certified values of the water standard has to be expected. This is also confirmed by the results obtained using other KF coulometric reagents, as illustrated in Application Note M655 [2].
- Recovery rates higher than 100% are mainly achieved with the generator cell without diaphragm. It is conceivable that its geometry may affect the determination, as indicated by other measurements using generator cells with and without diaphragm [3, 4].

Repeatability

- For the 1 mg/g standard, the precision – expressed as the relative standard deviation srel in % – is very good, with results varying ranging from 0.2% up to 0.6%.
- For the 0.1 mg/g standard, the same trend as for the 1 mg/g standard is observed;: since the water amount is lower, a higher deviation can be observed, i.e., srel ranging from srel 0.8% up to 3.1%.

Amount of electrolyte

- When titrating fresh coulometric electrolyte, the first 2-3 results are generally deviating. With increasing number of samples, the values are approaching the certified values. Thus, it is recommended to run several samples.
- However, if too many sample series are titrated in the same electrolyte, the level in the anolyte compartment is increasing. This is affecting the results since the stirring action is not efficient anymore. Thus, the higher the electrolyte level in the cell, the lower the recovery rate will be in general, especially for the 0.1 mg/g standard.

Waste Disposal and Safety Measures

Wear personal protection, i.e., safety glasses, lab coats and gloves. Read and understand the MSDS's when prior to using any chemicals prior to use. Dispose the solutions as organic solvents.

Literature

[1] "Water Content Determination in Water Standard 1.0 mg/g", METTLER TOLEDO Titration Application Note no. M314.

[2] "Water Content Determination in Water Standard 0.1 mg/g", METTLER TOLEDO Titration Application Note no. M655.

[3] A. Aichert, C. A. De Caro, "Coulometric Karl Fischer Titration", 2017, p. 18, (PDF) Coulometric Karl Fischer Titration (researchgate.net).

[4] M. Lanz, C. A. De Caro, K. Rüegg, A. De Agostini, "Coulometric Karl Fischer titration with a diaphragm-free cell: Cell design and applications", Food Chemistry 96(3), pp. 431-435, 2006.

Further Information

▸ **Titrator Compact C30SX | Coulometric KF Titrators**

Measured Values

HYDRANAL™ Water Standard 1.0 mg/g – C30S without diaphragm – (M904A) - Aquagent® Coulometric AG

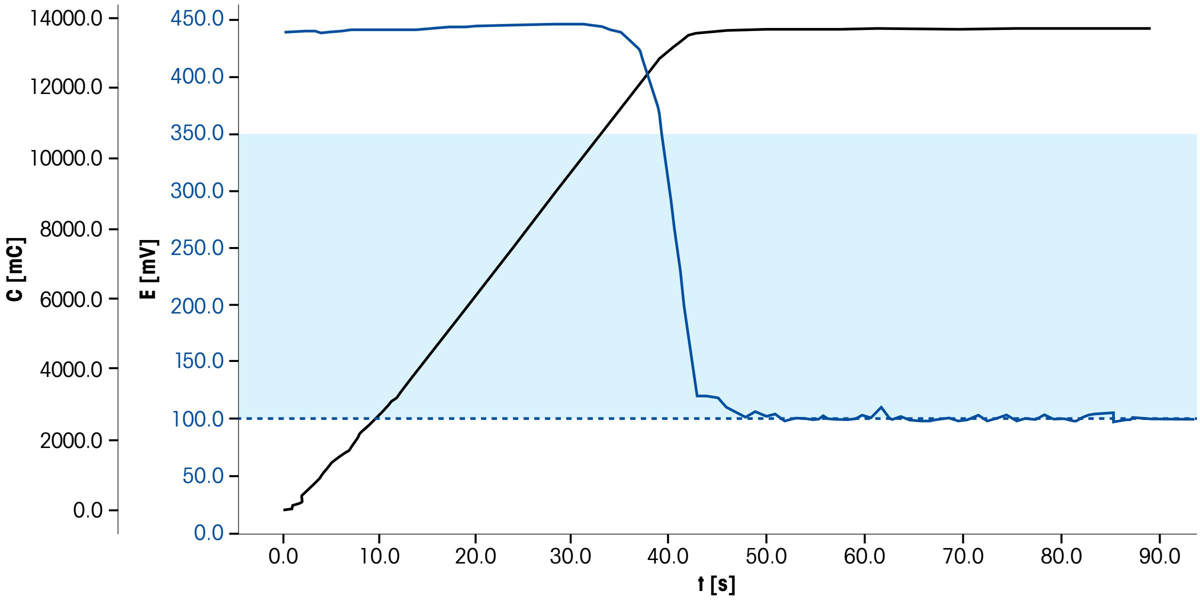

Figure 3: Karl Fischer E-t titration curve (blue) and C-t (grey) of 1 mg/g liquid water standard measured with a generator electrode without diaphragm.

Time [s]	C [mC]	E [mV]	Drift [µg/min]	H_2O [µg]
0	0	438.2	0	0
1	31.8	438.7	13.2	3
1	116.9	438.6	92.4	10.9
2	221.2	439.1	224.1	20.6
2	413.6	438.3	378.2	38.6
3	659.8	439.1	601.6	61.6
4	959.7	437.9	833.1	89.6
…	…	…	…	…
33	10693.8	443.2	1904	998.3
35	11400.8	438	1939.5	1064.3
37	12107.8	422.8	1970.7	1130.3
39	12814.8	368.3	1997.7	1196.3
41	13286.1	240.8	2021.5	1240.3
42	13496.5	172	1236.6	1259.9
…	…	…	…	…
86	13700.7	97.3	0	1279
88	13700.7	100	0	1279
88	13703.7	101.3	0	1279.3
90	13703.8	99.9	10.8	1279.3
90	13703.8	94.9	0	1279.3

HYDRANAL™ Water Standard 0.1 mg/g – C30S without diaphragm (M904B) – Aquagent® Coulometric AG

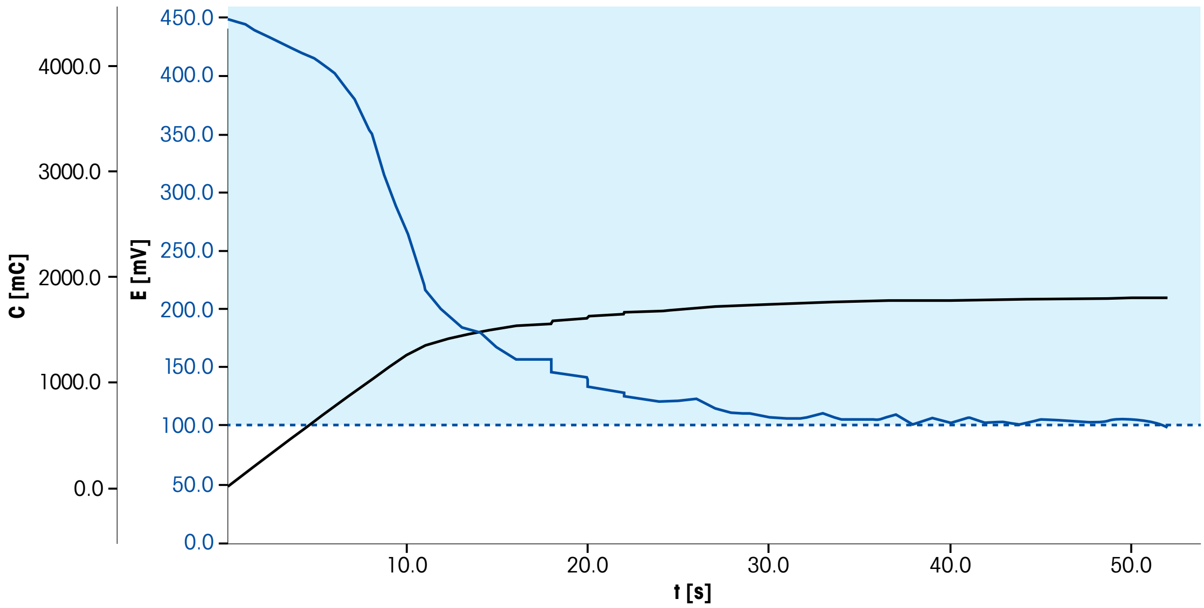

Figure 4: Karl Fischer E-t titration curve (blue) and C-t (grey) of 0.1 mg/g liquid water standard measured with a generator electrode without diaphragm.

Time [s]	**C** [mC]	**E** [mV]	**Drift** [µg/min]	**H_2O** [µg]
0	0	449.1	0	0
1	128.7	444.2	361.1	12
2	257.3	435.2	730.8	24
3	385.8	428.2	886.9	36
4	514.4	420.6	968.9	48
5	642.9	413.6	1017.7	60
6	769.8	401.8	1047.3	71.9
7	895.9	381.6	1066	83.6
8	1018.8	351	1052.7	95.1
9	1138.4	301.7	1031.9	106.3
10	1252.3	265	1003	116.9
11	1345.9	216.5	943.2	125.6
12	1399.7	197.8	735.1	130.7
13	1442	184.5	545.2	134.6
…	…	…	…	…
49	1792.8	104.5	0	167.4
50	1795.4	105.3	0	167.6
51	1797.1	103.4	0	167.8
52	1798	98.9	0	167.8
52	1798	98.9	0	167.8

Methods – 1 mg/g and 0.1 mg/g

001	Title	
	Type	KF titration Coul.
	Compatible with	C30S/T7/T9
	ID	M904A
	Title	Water standard 1.0 mg/g

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002	Sample	
	Sample	
	Number of IDs	1
	ID 1	--
	Entry type	Weight
	Lower limit	0.0 g
	Upper limit	2.0 g
	Density [g/mL]	1.0
	Correction factor	1.0
	Temperature	25.0 °C
	Autostart	Yes
	Entry	After addition

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003	Titration stand	
	Type	KF stand
	Titration stand	KF stand
	Source for drift	Online
	Max. start drift	25 µg/min

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004	Mix time	
	Duration	15 s

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005	Titration (KF Coul) [1]	
	Sensor	
	Type	Polarized
	Sensor	DM143-SC
	mV	mV
	Indication	Voltametric
	Ipol	5.0 µA
	Stir	
	Speed	45 %
	Control	
	Endpoint	100.0 mV
	Control band	250.0 mV
	Rate	Normal
	Generator current	Automatic
	Termination	
	Type	Drift stop relative
	Drift	3.0 µg/min
	Min. time	90 s
	Max. time	3600 s

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006	Calculation R1 (Content)	
	Result type	Predefined
	Result	Content
	Result unit	mg/g
	Formula R1 =	(ICEQ/10.712-TIME*DRIFT)*C/m
	Constant C =	1000
	Decimal places	3

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007	Calculation R2 (Recovery)	
	Result type	User defined
	Result	Recovery
	Result unit	%
	Formula	R2 = (R1/H[H])*100
	Constant	C = 1
	Decimal places	3

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008	End of sample	
	Open series	Yes

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001	Title	
	Type	KF titration Coul.
	Compatible with	C30S/T7/T9
	ID	M904B
	Title	H2O std 0.1 mg/g

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002	Sample	
	. . . .	
	Lower limit	1.0 g
	Upper limit	2.5 g

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003 | Titration stand

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004 | Mix time

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005	Titration (KF Coul) [1]	
	. . . .	
	Control	
	Endpoint	100.0 mV
	Control band	400.0 mV
	Rate	Cautious
	Generator current	Fix
	Current	200 mA
	Termination	
	Type	Drift stop relative
	Drift	3.0 µg/min
	Min. time	30 s
	Max. time	90 s

006 | Calculation R1 (Content)

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007 | Calculation R2 (Recovery)

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008	End of sample	
	Open series	Yes

METTLER TOLEDO Group
Analytical
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For more information

30959269 / M904 v1.0 CDC
Group MarCom RITM1164596 NM