Karl Fischer water determination in non-explosive gases

Of interest to:
General analytical laboratories

Summary

This Application Bulletin describes the determination of water in non-explosive and non-flammable gaseous samples with the coulometric Karl Fischer method. This method is ideal for very low water contents.

Apparatus and accessories

- 2.756.0010 KF Coulometer, cell with diaphragm, including 728 Magnetic Stirrer
- 2.731.0010 Relay Box
- 6.2148.010 Remote Box
- 2.846.0010 Dosing interface
- 6.1439.020 Gas inlet tube with frit
- 6.1805.010 FEP tubing/ M6/ 13 cm
- 6.2811.000 Molecular sieve 0.3 nm
- 6.2151.000 Cable (Dosing Interface – PC)
- 6.2125.100 Cable (Relay Box)
- 2 x Magnetic valve, Lucifer
- T-distribution connector 6 mm MS, Swagelock
- Copper tubing 2 m, 4 x 6 mm
- 4 x Connector 6 mm x ¼ " MS, Swagelock
- Connector ¼ " x ⅛", Swagelock
- Flow controller Red-y smart controller GSC (Vögtlin Instruments AG, Aesch (CH))
- Pressure meter Bioblock Scientific MP 340A 0...2000 mbarA
- 6.6056.112 ***tiamo*** full 1.1

Remark: For gases with a high water content (> 50 ppm), a generator electrode without diaphragm can be used. For gases with a water content below 50 ppm, a generator electrode with diaphragm has to be used, otherwise the results will be too high.

Reagents

- Anolyte: Hydranal-Coulomat AG Oven, Sigma-Aldrich 34739
- Catholyte: Hydranal-Coulomat CG, Sigma-Aldrich 34840

Setup

See Appendix

Parameters

Start drift	:	5 µg/min
Extraction time	:	15 min
Drift correction	:	automatic
Stop criterion	:	rel. drift
Relative stop drift	:	5 µg/min

Stirrer

Speed : 6

The stirrer speed should be set high enough to obtain thorough mixing of the gas bubbles with the KF reagent. Too strong stirring of the solution may, however, affect the drift value. For vessel contents between 110 and 200 mL, a stirring speed of 6 is recommended.

Karl Fischer reagent

110...200 mL

Volumes larger than 200 mL KF reagent make it difficult to reach a low start drift. Less than 110 mL is not enough to make all the gas react with the solution.

Gas settings

Gas pressure at the cylinder: at least 2 bar (200 kPa)

Gas flow rate: at least 200 mL/min

Analysis

Prior to the analysis, the whole system should be purged with the gas to be measured. Several liters of gas may be needed for a complete rinsing. The gas tubing and valves should be rinsed until a stable water content is reached.

During the extraction time, valve 1 is closed and valve 2 is opened to let the gas enter the titration cell. At the end of the extraction time, valve 2 is closed and valve 1 is opened. In this way the gas lines are constantly rinsed with gas and no water enters the tubing.

Remark: If measurements are performed over several days, conditioning of the reagent should not be interrupted during the whole period.

No blank measurements were carried out as the blank values are equal to the drift. Therefore, only a drift correction was applied.

Calculation

$V_1 = t \cdot \Phi$ (1)

$$m_{Gas}\ [mg] = 1000 \cdot \frac{V_1 \cdot M \cdot T_0 \cdot P_1}{V_0 \cdot (T_0 + \theta_1) \cdot P_0} \quad (2)$$

$$H_2O\ [ppm] = 1000 \cdot \frac{m_1}{m_{Gas}} \quad (3)$$

m_1 = absolute water content [µg]
Φ = gas flow rate [L/min]
t = extraction time [min]
V_1 = added gas volume [L]
V_0 = gas volume at 0 °C = 22.4 L/mol
T_0 = 273.15 K
θ_1 = gas temperature [°C]
M = molar mass of gas [g/mol]
P_1 = absolute gas pressure at θ_1 [kPa]
P_0 = gas pressure at T_0 = 101.325 kPa

Remark: For a correct calculation of the water content, a pressure correction should be applied, especially for gases with a low water content.

Results

The detection limit of this method was found to be around 2 ppm. The determination limit was approximately 5 ppm.

Relative standard deviations with nitrogen gas were found to lie between 5 and 6%.

Remarks

- As magnetic valves are used, this setup is not suitable for explosive gases.
- A good repeatability can only be obtained with a precise flow meter and pressure meter.
- The setting used is different from the one stipulated in the ISO 10101-3:1993 standard. The flowmeter used in the ISO norm contains water, which means that the gas must be dried before entering the flow meter. Accordingly, the flow rate has to be measured after the cell. However, the measured flow rate is reduced by a factor of 2 compared to a measurement before the titration cell.

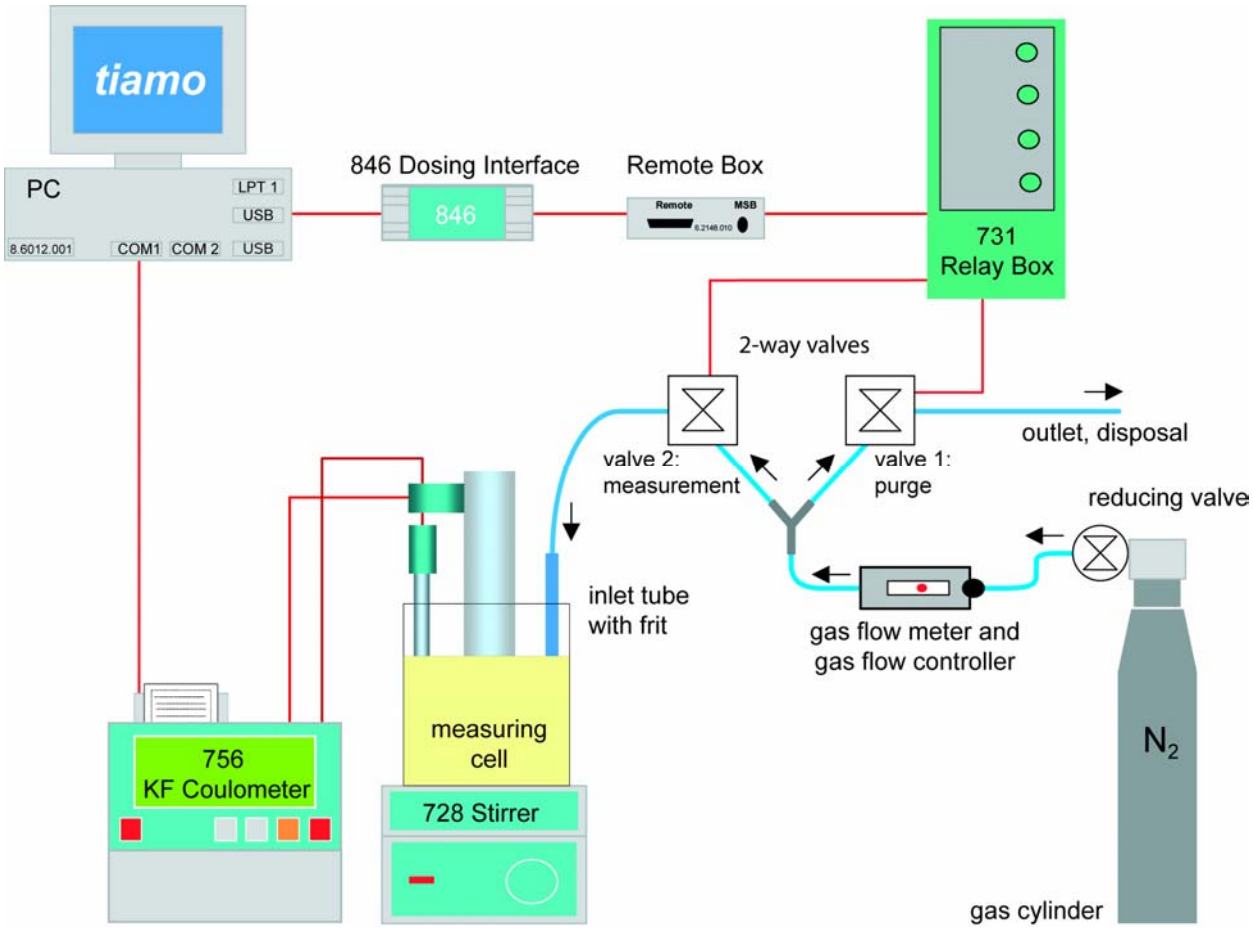
Literature

ISO 10101-3:1993

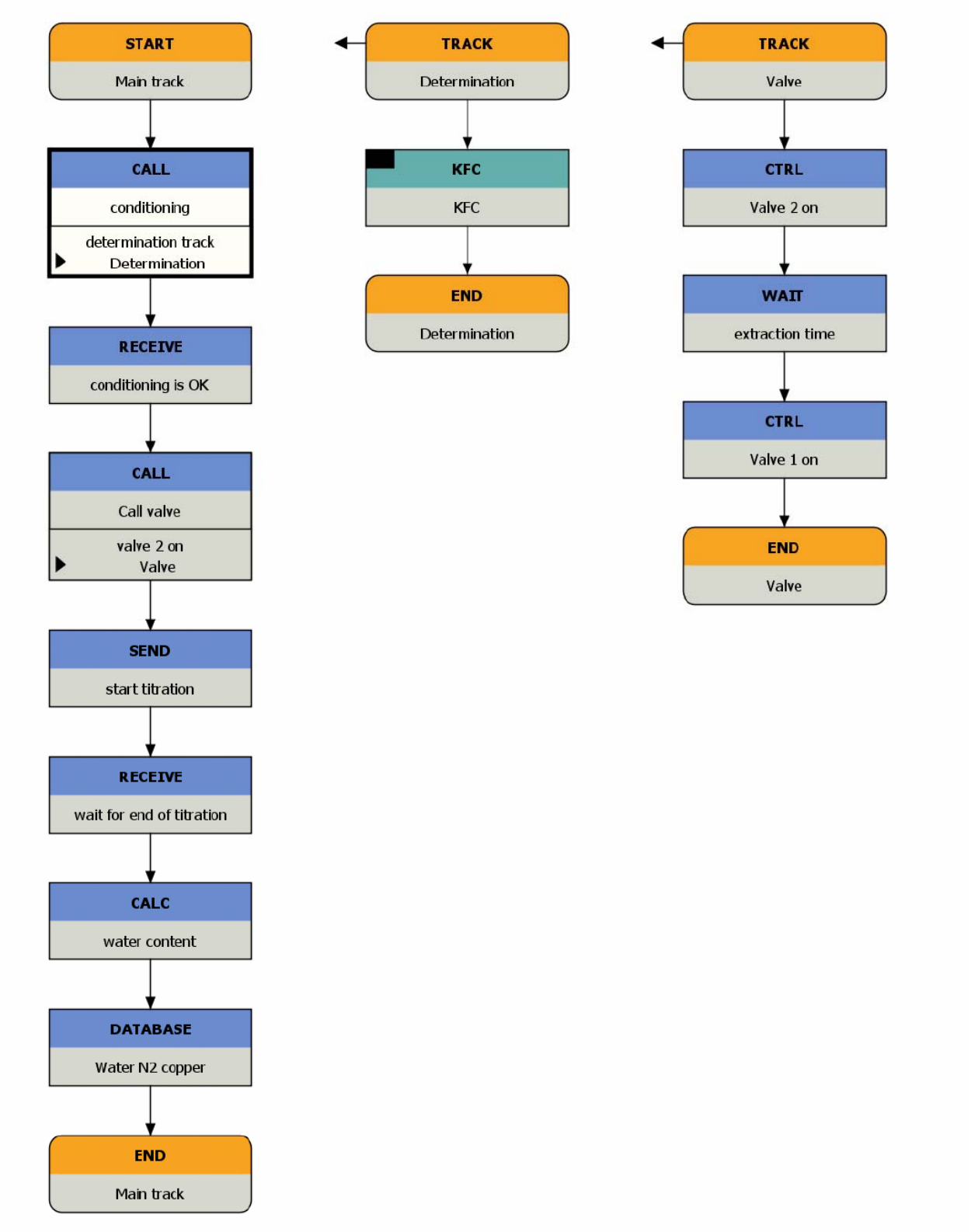
Natural gas – Determination of water by the Karl Fischer method – Part 3: Coulometric procedure

Appendix

Instrument setup



Caution: the valves heat up to 75 °C!


START
Main track
CALL
conditioning
determination track
Determination
RECEIVE
conditioning is OK
CALL
Call valve
valve 2 on
Valve
SEND
start titration
RECEIVE
wait for end of titration
CALC
water content
DATABASE
Water N2 copper
END
Main track
TRACK
Determination
KFC
KFC
END
Determination
TRACK
Valve
CTRL
Valve 2 on
WAIT
extraction time
CTRL
Valve 1 on
END
Valve

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	RES-NB		
User	res	2006-09-04	15:55:52 UTC+2

Method parameters

Method . . . . . Water N2 15 min cond 10
Method saving date . . . . . 2005-05-17 09:49:31 UTC+2
Method version 1
Method group . . . . . Main group
Method status . . . . . original
Method saved by (full name) . . . . .
Method saved by (short name) . . . . . esch

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Determination
Live display 2 . . . . . Main track
Statistics . . . . . on
Number of single determinations 3
Conditioning
Automatic conditioning . . . . . off

Application note

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2			off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off

Mail to	
Subject	Meldung von tiamo - Methode 'Neue Methode 1' - Befehl 'Hauptspur'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample position**
Type	Number
Assignment	on Sample position
Value	off
Check at start	on
Comment	Sample position number
Variable monitoring	off
Lower limit	
Upper limit	
Message	
Display message	on
Record message	on
Message by e-mail	off
Mail to	
Subject	Meldung von tiamo - Methode 'Neue Methode 1' - Befehl 'Hauptspur'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample size unit**
Type	Text
Assignment	on Sample size unit
Value	off
Check at start	on
Comment	Sample size unit

Name	**ID1**
Type	Text
Assignment	on ID1

Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off
Check at start . . . . . off
Comment

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 3

CALL **conditioning**

Call text	Track name	Condition	Condition
determination track	Determination	off	

RECEIVE **conditioning is OK**

Wait for event/status

Wait until all conditions are met . . . . . on
Wait until one of the conditions is met . . . . . off

Command	Event message	Comment
KFC	Condok	

Timeout . . . . . off

Message

CALL **Call valve**

Call text	Track name	Condition	Condition
valve 2 on	Valve	off	

SEND **start titration**

Send event messages

Receiver	Selection	Event message	Comment
Command	KFC	Start Titration	

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License ID 124049905 Program version tiamo 1.1 - 36
Client name RES-NB
User res 2006-09-04 15:55:52 UTC+2

RECEIVE **wait for end of titration**

Wait for event/status

Wait until all conditions are met . . . . . on
Wait until one of the conditions is met . . . . . off

Command	Event message	Comment
KFC	Finished	

Timeout . . . . . on
Time . . . . . 30 min

Message

CALC **water content**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
water abs	= 'KFC.EP.QTY'	µg	4	RS01	off
N2 mass	= (15.1 * 'CV.Flowrate' * 273.15 * 28.01) / (22.4 * (273.15 + 25))	mg	2	RS02	off
water %	=0.1 * 'KFC.EP.QTY' / 'RS.N2 mass'	%	4	RS04	off
water ppm	=1000 * 'KFC.EP.QTY' / 'RS.N2 mass'	ppm	1	RS03	off
Startdrift	= 'KFC.DRI'	µg/ min	1	RS05	off
H2O	='KFC.LP.QTY'	µg	2	RS06	off
Total duration	= 'KFC.DBL'	s	1	RS07	off

Result name . . . . . **water abs**
Formula . . . . . = 'KFC.EP.QTY'
Unit . . . . . µg
Decimal places 4
Assignment RS01
Statistics . . . . . off
Description . . . . . RS.'Resultatname'[.VAL]Resultatwert.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **N2 mass**
Formula . . . . . = (15.1 * 'CV.Flowrate' * 273.15 * 28.01) / (22.4 * (273.15 + 25))
Unit . . . . . mg
Decimal places 2
Assignment RS02
Statistics . . . . . off
Description . . . . . RS.'Resultatname'[.VAL]Resultatwert.

Result monitoring	off
Save result as common variable	off
Name	
Save result as titer	off
Solution name	

Result name	**water %**
Formula	=0.1 * 'KFC.EP.QTY' / 'RS.N2 mass'
Unit	%
Decimal places	4
Assignment	RS04
Statistics	off
Description	RS.'Resultatname'[.VAL]Resultatwert.
Result monitoring	off
Save result as common variable	off
Name	
Save result as titer	off
Solution name	

Result name	**water ppm**
Formula	=1000 * 'KFC.EP.QTY' / 'RS.N2 mass'
Unit	ppm
Decimal places	1
Assignment	RS03
Statistics	off
Description	RS.'Resultatname'[.VAL]Resultatwert.
Result monitoring	off
Save result as common variable	off
Name	
Save result as titer	off
Solution name	

Result name	**Startdrift**
Formula	= 'KFC.DRI'
Unit	µg/ min
Decimal places	1
Assignment	RS05
Statistics	off
Description	RS.'Resultatname'[.VAL]Resultatwert.
Result monitoring	off
Save result as common variable	off
Name	
Save result as titer	off
Solution name	

Result name	**H2O**
Formula	='KFC.LP.QTY'

Unit . . . . . µg
Decimal places 2
Assignment RS06
Statistics . . . . . off
Description . . . . . RS.'Resultatname'[.VAL]Resultatwert.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **Total duration**
Formula . . . . . = 'KFC.DBL'
Unit . . . . . s
Decimal places 1
Assignment RS07
Statistics . . . . . off
Description . . . . . RS.'Resultatname'[.VAL]Resultatwert.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

DATABASE **Water N2 copper**

Database

Water N2 copper

TRACK **Determination**
Return immediately . . . . . on
Delete all data . . . . . on

KFC **KFC**
General/Hardware
Device
Device name . . . . . 831_1
Indicator electrode
I(pol) . . . . . 10 µA
Electrode test . . . . . on
Generator electrode
Generator type . . . . . with diaphragm
Generator current . . . . . auto mA
Stirrer
Switch on/off automatically . . . . . on
Start conditions

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License ID 124049905 Program version tiamo 1.1 - 36
Client name RES-NB
User res 2006-09-04 15:55:52 UTC+2

Pause
Pause . . . . . 0 s

Control parameters

End point
EP at . . . . . 50.0 mV

Control
Dynamics . . . . . 70 mV
Max. rate . . . . . maximum µg/min
Min. rate . . . . . 15.0 µg/min

Stop criterion
Stop criterion . . . . . rel. drift
Relative stop drift . . . . . 5 µg/min

Titration parameters

Extraction time . . . . . 900 s
Temperature . . . . . 25.0 °C
Time interval measuring point . . . . . 2 s

Stop conditions

Stop time . . . . . off s

Conditioning

Conditioning . . . . . on
Start drift . . . . . 10 µg/min
Drift correction . . . . . automatic
Delay after 'Cond ok' . . . . . 60 s
Only start titration by a start command from a SEND command . . . . . on
Show measured value during conditioning . . . . . on

Additional evaluations

Fix end point evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

TRACK **Valve**

Return immediately . . . . . on
Delete all data . . . . . off

CTRL **Valve 2 on**

Device
Device name . . . . . 808_1
Remote box 1

Set lines
Output signal **********1**

WAIT **extraction time**

Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 906

Unit . . . . . s
Message
Record message . . . . . on
Message by e-mail . . . . . off
Acoustic signal . . . . . off

CTRL **Valve 1 on**
Device
Device name . . . . . 808_1
Remote box 1
Set lines
Output signal **********0**