



Water in Diesel fuel

Karl Fischer application

Product group

Hydrocarbons, Petroleum products

General Information concerning the product group

Hydrocarbons

Saturated hydrocarbons can in most cases be titrated according to standard methods. To overcome solubility problems of unpolar or weakly polar substances, the addition of a solubiliser to the solvent is necessary. In the case of long-chain and cyclic hydrocarbons, long-chain alcohols (e.g. propyl alcohol or decyl alcohol) or chloroform are thus recommended. Toluene, xylene or chloroform improve the solubility of aromatic compounds.

Unsaturated hydrocarbons can usually be titrated in the same way. Interferences due to double bonds only occur with some very reactive compounds. In the case of interferences (unstable end point or none at all) a methanol-free, alcoholic solvent (e.g. CombiSolvent or CombiSolvent Keto) should be utilised instead of methanol.

Recommended methods are both the volumetric titration with one or two component reagents, as well as the coulometric analysis. The latter is predominantly applied for low water concentrations (< 0.1 %).

Petroleum products

Petroleum products are mixtures of long-chain or aromatic hydrocarbons. They are hardly soluble in methanol. Water determination by Karl Fischer therefore requires the addition of solubilisers. For light oils, long-chain alcohols are suitable. For dissolving of heavier oils toluene, xylene or chloroform are added. For the volumetric titration specific KF solvents for oils are available. Due to the very low water concentration titrants with a low factor (2 mg/ml or 1 mg/ml) are recommended.

During coulometric determination without diaphragm 20% solubiliser can be added to the working medium, or 40% solubiliser to the analyte in the case of coulometry with diaphragm.

Note that oils are often heterogeneous compounds with uneven distribution of water and should thus be homogenised (e.g. with Ultra-Turrax) prior to KF determination.

Additives in oils can cause side reactions during KF determination. Here, the direct coulometric analysis is not possible, the volumetric titration only conditionally. As an alternative, the KF oven technique can be utilised in combination with coulometry, whereby the release of water is best achieved at temperatures between 120 and 140 °C.

Special Information concerning the sample and the methods

Water determination can be carried out volumetrically or coulometrically. Addition of solubilisers is necessary.



Application

Titration one component system

Reagents

Titrant:	Aquastar - CombiTitrant 2	188002	
	One component reagent for volumetric Karl Fischer titration, 1 mL = approx. 2 mg water		
Solvent:	Aquastar - CombiSolvent oils	188020	50 mL
	Solvent for volumetric Karl Fischer titration with one component reagents for oils		
or	Aquastar - CombiMethanol /	188009 /	30 mL / 20 mL
	Decanol	803463	
	solvent mixture for one component titration		

Titration parameters

Stirring time: 60 sec.

Default titration settings, e.g.:

$I(\text{pol}) = 20 - 50 \mu\text{A}$, $U(\text{EP}) = 100 - 250 \text{ mV}$

Stop criterion: drift < 20 $\mu\text{L}/\text{min}$

Sample size

5 mL

Procedure

The titration medium is first placed into the titration cell and titrated dry by means of the titrant. Then the sample is added with a syringe (exact sample weight determination by weighing of syringe before and after injection) or volumetric pipette and the titration is started. For complete dissolution of the sample a stirring time of 60 seconds is recommended.

Titration two component system

Reagents

Titrant:	Aquastar - Titrant 2	188011	
	Titrant for volumetric titration with two component reagents, 1 mL = approx. 2 mg water		
Solvent:	Aquastar - Solvent oils & fats	188016	40 mL
	Solvent for volumetric Karl Fischer titration with two component reagents for oils & fats		
and	Chloroform	102445	10 mL
	as solubiliser		

Titration parameters

Stirring time: 60 sec.

Default titration settings, e.g.:

$I(\text{pol}) = 20 - 50 \mu\text{A}$, $U(\text{EP}) = 100 - 250 \text{ mV}$

Stop criterion: drift < 20 $\mu\text{L}/\text{min}$

Sample size

5 mL

Procedure

The titration medium is first placed into the titration cell and titrated dry by means of the titrant. Then the sample is added with a syringe (exact sample weight determination by weighing of syringe before and after injection) or volumetric pipette and the titration is started. For complete dissolution of the sample a stirring time of 60 seconds is recommended.



Application

Coulometry with diaphragm

Reagents

Catholyte:	Aquastar - CombiCoulomat frit Coulometric Karl Fischer reagent for cells with diaphragm	109255	5 mL
Anolyte:	Aquastar - CombiCoulomat frit Coulometric Karl Fischer reagent for cells with diaphragm	109255	80 mL
and	Decanol as solubiliser	803463	40 mL

Titration parameters

Stirring time: 60 sec.

Default coulometer settings for cell with diaphragm:

For end point indication, e.g.:

$I(\text{pol}) = 5 - 10 \mu\text{A}$, $U(\text{EP}) = 50 - 100 \text{ mV}$

Stop criterion: drift < 10 $\mu\text{g}/\text{min}$

Sample size

1 mL

Procedure

The Karl-Fischer reagent is placed into the cathode and anode compartment of the titration cell with diaphragm. The coulometer is started and the solvent is titrated dry. After preliminary titration and stabilisation of drift the sample is injected into the titration cell with a syringe (exact sample weight determination by weighing of syringe before and after injection) and the water determination is started. For complete dissolution of the sample a stirring time of 60 seconds is recommended.

Coulometry without diaphragm

Reagents

Working medium:	Aquastar - CombiCoulomat fritless Coulometric Karl Fischer reagent for cells with or without diaphragm	109257	80 mL
and	Decanol as solubiliser	803463	20 mL

Titration parameters

Stirring time: 60 sec.

Default coulometer settings for cell without diaphragm:

For end point indication, e.g.:

$I(\text{pol}) = 5 - 10 \mu\text{A}$, $U(\text{EP}) = 50 - 100 \text{ mV}$

Stop criterion: drift < 10 $\mu\text{g}/\text{min}$

Sample size

1 mL

Procedure

The Karl-Fischer reagent is placed into the titration cell without diaphragm. The coulometer is started and the solvent is titrated dry. After preliminary titration and stabilisation of drift the sample is injected into the titration cell with a syringe (exact sample weight determination by weighing of syringe before and after injection) and the water determination is started. For complete dissolution of the sample a stirring time of 60 seconds is recommended.



Ordering Information

Product	Catalog No.
Chloroform for analysis EMSURE® ACS,ISO,Reag. Ph Eur	102445
CombiCoulomat frit Karl Fischer reagent for the coulometric water determination for cells with diaphragm Aquastar™	109255
CombiCoulomat fritless Karl Fischer reagent for coulometric water determination for cells with and without diaphragm Aquastar™	109257
CombiTitrant 2 one component reagent for volumetric Karl Fischer titration 1 ml □ ca. 2 mg H ₂ O Aquastar™	188002
CombiMethanol Solvent for volumetric Karl Fischer titration with one component reagents max. 0.01% H ₂ O Aquastar™	188009
Titrant 2 titrant for volumetric Karl Fischer titration with two component reagents 1 ml □ ca. 2 mg H ₂ O Aquastar™	188011
Solvent Oils & Fats Solvent for volumetric Karl Fischer titration with two component reagents for oils and fats Aquastar™	188016
CombiSolvent Oil Solvent for volumetric Karl Fischer titration with one component reagents for oils Aquastar™	188020
1-Decanol for synthesis	803463