

## HYDRANAL®-E – non-toxic Karl Fischer Titration

The Karl Fischer titration is a well-known method for water determination in various substances like chemicals, oils, pharmaceuticals or food. The determination of water content is used for monitoring the product quality and to ensure chemical and physical properties.



increased significantly and has become a topic of public discussion. Today, the main focus of the Riedel-de Haën R & D laboratory is the development of reagents without hazardous substances. At the center of the continuous developments is the replacement of toxic methanol, which is widely used as solvent in the titration vessel or as sol-

### HYDRANAL® – Pyridine-free Karl Fischer Reagents

In 1935 the German petrochemist Karl Fischer developed a titrimetric reagent for moisture determination containing pyridine, which is unpleasant to use and harmful. About 20 years ago, Eugen Scholz at Riedel-de Haën improved the Karl Fischer titration by replacing the pyridine with imidazole – the beginning of **HYDRANAL®**, the leading pyridine-free reagents for Karl Fischer titrations. The higher basicity of imidazole led to a faster reaction speed and more stable end-points. The replacement of pyridine by the non-toxic and odourless imidazole was the first step at Riedel-de Haën in developing reagents less harmful to health and to the environment. In the following years, Riedel-de Haën launched a wide range of reagents for volumetric and coulometric titrations, leading to the worldwide success of **HYDRANAL®**.

### The non-toxic Generation – HYDRANAL®-E Types

During the last two decades, the need for environmental protection and safety regulations has

vent for Karl Fischer reagents, by the non-toxic ethanol (figure 1). Changing to the higher homologous ethanol has turned out to be a challenging task. Ethanol has not been used in the past for Karl Fischer reagents for two important reasons. The speed of the Karl Fischer reaction in pure ethanol is very slow and the electrochemical behavior varies – the conductivity of ethanol is lower.

The first problem could be solved by adding accelerators to the ethanol which do not interfere with the Karl Fischer titration. The additives accelerate the reaction and the titration can be carried out in a shorter time than in methanol. Second, the conductivity for a coulometric reagent can be adjusted. A patent is pending for these developments. As a result of this continuous research work, the new

**HYDRANAL®-E** types represent the first non-toxic Karl Fischer reagent line for the volumetric and the coulometric titration.

**HYDRANAL®-E**  
the new dimension  
in non-toxic  
Karl Fischer titration

### Contents:

- **Pyridine-free Karl Fischer Reagents**
- **The non-toxic Generation – HYDRANAL®-E Types**
- **Comparison with traditional Methanol based Reagents**

### Information concerning the Toxicity of Methanol:

Methanol can be absorbed through the respiratory ducts or the skin. According to the literature, this can be significant. In general, methanol poisoning can be divided into several stages.

First, a narcotic effect occurs and, in comparison with ethanol, the biotransformation process of methanol is slower.

Later, formic acid, which is formed through enzymatic oxidation of methanol, inhibits vesicular breathing. Typical symptoms in this phase are difficulty breathing, and in extreme cases of methanol exposure, paralysis can lead to death.

Nearly parallel to these initial symptoms, the third stage progresses by disturbing the victim's vision. In the beginning phase, this effect is reversible.

In more severe cases, irreversible blindness can result.

### The non-toxic HYDRANAL®-E Types

#### Volumetric One-Component Titration

**HYDRANAL®-Composite** is the most frequently used pyridine-free reagent worldwide for Karl Fischer titration. The reagent contains all the reactants for the volumetric Karl Fischer titration of water, e.g. iodine, sulfur dioxide and imidazole, dissolved in a suitable solvent. A mixture of imidazole and 2-methylimidazole buffers the sulphur dioxide. The reagent is not declared as toxic or flammable and it is not an irritant to the skin or eyes. Studies have been made under GMP conditions to prove the properties of this reagent. Regarding these results the use of **HYDRANAL®-Composite** is not dangerous to health. Methanol is usually used as solvent for the one-component titration. Instead of methanol, **HYDRANAL®-CompoSolver E** can be used. This new reagent is non-toxic because it contains ethanol.

#### Volumetric Two-Component Titration

The **HYDRANAL®-two-component system** consisting of **HYDRANAL®-Titrant** and **HYDRANAL®-Solvent** is distinguished by a high rate of titration, a stable end-point and a high

accuracy of the results obtained. The

**HYDRANAL®-Solvent** serves as the working medium and the **HYDRANAL®-Titrant** is used as the titrating agent and is administered to the titration vessel from the burette. These reagents can be used with all commercially available equipment. Non-toxic volumetric reagents have been developed for the two-component-system as well. **HYDRANAL®-Solvent E/Titrant E** are based on the new ethanol formulation instead of methanol. With **HYDRANAL®-Titrant 2 E** and **-Titrant 5 E**, two different titers are available. The new Solvent E/Titrant E system guarantees adequate properties in comparison to our traditional reagent types.

#### Coulometric Titration

Coulometry is principally intended for the determination of water in substances with low water contents (0.0001–0.1%). Particular advantages are to be seen in the lower ppm range. This is a micromethod and therefore the ideal complement to volumetric titration methods for smaller amounts of water.

**HYDRANAL®-Coulomat E** contains the same ingredients as Coulomat AG, but methanol is replaced by ethanol. An additional benefit is that the reagent can be used as both anolyte and catholyte for the cell with a diaphragm. A special dedicated catholyte is no longer necessary.

**HYDRANAL®-Coulomat E** can also be used in the cell without a diaphragm.

### E-Types in Comparison to Methanol based Karl Fischer Reagents

#### Volumetric One-Component Titration

In general most of the applications for reagents based on methanol are transferable to the ethanol based reagents. **HYDRANAL®-CompoSolver E** shows distinct advantages. For example, the titration time in this reagent is much shorter than in pure methanol. Additionally ketones like acetone can also be investigated and the solubility for long-chained hydrocarbons is improved. An additional solubilizer like chloroform is no longer necessary. Figure 2 shows the quantity of different organic samples which can be dissolved in 30 ml **HYDRANAL®-reagent**.

If methanol is used as solvent the determination of water in aldehydes and ketones is affected. In a side-reaction, acetals and ketals are formed, water is the by-product. This results in vanishing end-points and erroneously high water contents or no adjusting end-points. The side reaction can be suppressed using the well-known **HYDRANAL®-Composite 5K, -Working Medium K** or **-KetoSolver**. Furthermore, ketones like acetone or methyl-iso-butylketone can be analysed in **HYDRANAL®-CompoSolver E**.

Figure 3 shows the titration of 5 ml acetone. In

Figure 1:  
Declaration of **HYDRANAL®-reagents** based on methanol and the **HYDRANAL®-E** types.

Reagents based on methanol	Non-toxic HYDRANAL®-E types
<b>Volumetric titration: one-component reagents</b>	
HYDRANAL®-Composite, declaration is not demanded used in conjunction with HYDRANAL®-Methanol dry, <b>toxic</b>	HYDRANAL®-Composite, declaration is not demanded used in conjunction with HYDRANAL®-CompoSolver E
<b>Volumetric titration: two-component reagents</b>	
HYDRANAL®-Solvent, <b>toxic</b> HYDRANAL®-Titrant 5, <b>toxic</b> HYDRANAL®-Titrant 2, <b>toxic</b>	HYDRANAL®-Solvent E, <b>harmful</b> HYDRANAL®-Titrant 5 E HYDRANAL®-Titrant 2 E
<b>Coulometric titration</b>	
HYDRANAL®-Coulomat AD, <b>toxic</b> HYDRANAL®-Coulomat AG, <b>toxic</b>	HYDRANAL®-Coulomat E, <b>harmful</b>

Every **HYDRANAL®-reagent** except **HYDRANAL®-Composite** is additionally declared as flammable. These declarations have been provided according to the European law, adapting to technical progress for the 25th Council Directive 67/548/EEC.

methanol a strong side reaction takes place and no end-point is found. In **HYDRANAL**<sup>®</sup>-Compo-Solver E the titration indicates a stable end-point. Actually a second 5 ml portion of acetone could be added.

### Volumetric Two-Component Titration

The characteristics of the **HYDRANAL**<sup>®</sup>-E types are very similar to the methanol-based Solvent / Titrant combination. The shelf life of the **HYDRANAL**<sup>®</sup>-Titrant E-reagents is identical to the Titrant reagents. Additionally there is no difference between the titer of **HYDRANAL**<sup>®</sup>-Titrant 5 / -Titrant 5 E and -Titrant 2 / -Titrant 2 E. In volumetric Karl Fischer titration generally the reagents of a 2-component-system react very fast. The reaction speed of **HYDRANAL**<sup>®</sup>-Solvent E / -Titrant 5 E compared with -Solvent / -Titrant 5 is identical. This is illustrated in the pre-titration shown in figure 4.

### Coulometric Titration

In coulometric Karl Fischer titration **HYDRANAL**<sup>®</sup>-Coulomat CG is used as catholyte in conjunction with -Coulomat AG. The new non-toxic **HYDRANAL**<sup>®</sup>-Coulomat E can be used as catholyte as well and it can be used as a one-component reagent for coulometric cells with a diaphragm. In figure 5, the analytical results of a validation for coulometric measurements with different Karl Fischer coulometers are shown. Corresponding to these results all combinations of **HYDRANAL**<sup>®</sup>-reagents have a high accuracy of the mean and high precision with standard deviations less than 0.5%.

	One-Component Reagents		Two-Component Reagents	
	CompoSolver E	Methanol	Solvent E	Solvent
Benzine	> 30 ml	> 30 ml	> 30 ml	10 ml
Petrolbenzine	> 30 ml	22 ml	30 ml	22 ml
n-Hexane	> 30 ml	13 ml	22 ml	7 ml
Cyclohexane	> 30 ml	11 ml	24 ml	6 ml
iso-Octane	> 30 ml	10 ml	18 ml	4 ml
1-Decane	> 30 ml	6 ml	12 ml	2 ml
1-Tetradecane	25 ml	1 ml	3 ml	< 1 ml
Dodecane	21 ml	< 1 ml	3 ml	< 1 ml

Figure 2: Comparison of the solubility of organic samples in 30 ml **HYDRANAL**<sup>®</sup>-reagent.

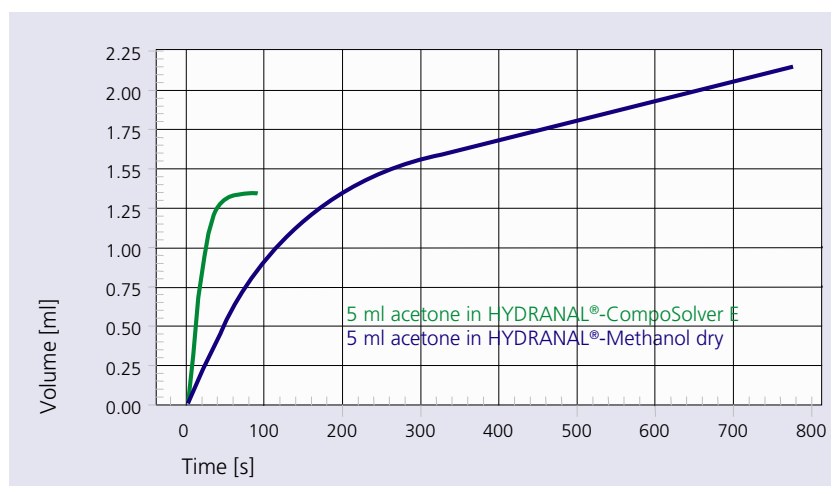


Figure 3: Determination of water in 5 ml acetone, titration with **HYDRANAL**<sup>®</sup>-CompoSolver E and **HYDRANAL**<sup>®</sup>-Methanol dry.

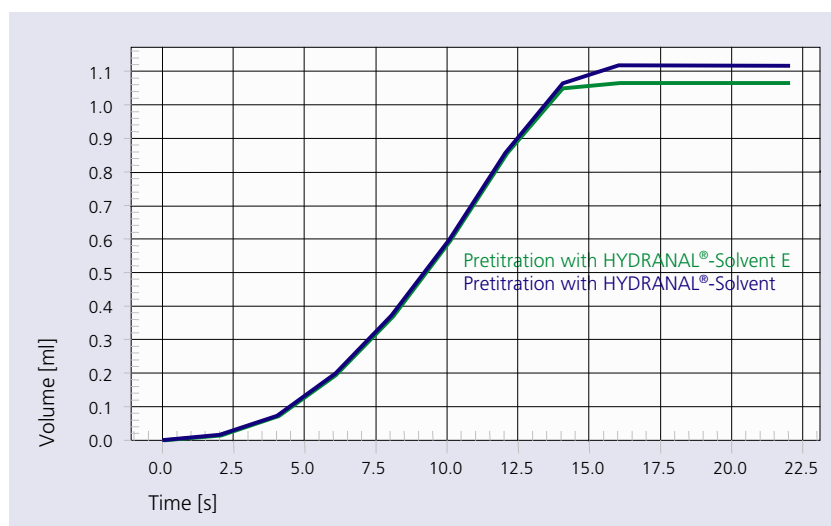


Figure 4: Pre-titration with **HYDRANAL**<sup>®</sup>-Solvent E / -Titrant 5 E compared with **HYDRANAL**<sup>®</sup>-Solvent / -Titrant 5.

Karl Fischer Titrator	Coulometer 1	Coulometer 2	Coulometer 3
Coulomat AG / CG	4992 µg ± 3 µg	4999 µg ± 22 µg	–
Coulomat E / CG	4999 µg ± 2 µg	4996 µg ± 1 µg	–
Coulomat E / E	4999 µg ± 7 µg	5021 µg ± 1 µg	5009 µg ± 10 µg

Figure 5: Survey of the high accuracy of several combinations of **HYDRANAL**<sup>®</sup>-reagents. For each test 10 x 5000 µg of water have been injected.

## Product Range of HYDRANAL®-Reagents

### Volumetric Karl Fischer titration – One-component reagents

Cat. No.	Product	Description	Pack Size
34805	HYDRANAL®-Composite 5	One component reagent, titer: 1 ml ~ 5 mg water	500 ml; 1 l; 2.5 l
34806	HYDRANAL®-Composite 2	One component reagent, titer: 1 ml ~ 2 mg water	500 ml; 1 l; 2.5 l
34827	HYDRANAL®-Composite 1	One component reagent, titer: 1 ml ~ 1 mg water	500 ml; 1 l
34816	HYDRANAL®-Composite 5K	One component reagent for titration in aldehydes and ketones, titer: 1 ml ~ 5 mg water	500 ml; 1 l
34734	HYDRANAL®-CompoSolver E	Methanol free working medium	1 l; 2.5 l
34817	HYDRANAL®-Working Medium K	To use with HYDRANAL®-Composite for titration of aldehydes and ketones	1 l
34738	HYDRANAL®-KetoSolver	To use with HYDRANAL®-Composite for titration of aldehydes and ketones	1 l; 500 ml
37855	HYDRANAL®-LipoSolver CM	To use with HYDRANAL®-Composite for titration of non polar substances	1 l
37856	HYDRANAL®-LipoSolver MH	To use with HYDRANAL®-Composite for titration of non polar substances, fats and oils	1 l

### Volumetric Karl Fischer titration – Two-component reagents

Cat. No.	Product	Description	Pack Size
34732	HYDRANAL®-Titrant 5 E	Methanol free titrant to use with HYDRANAL®-Solvent or HYDRANAL®-Solvent E	500 ml; 1 l; 2.5 l
34801	HYDRANAL®-Titrant 5	To use with HYDRANAL®-Solvent or HYDRANAL®-Solvent E	500 ml; 1 l; 2.5 l
34723	HYDRANAL®-Titrant 2 E	Methanol free titrant to use with HYDRANAL®-Solvent or HYDRANAL®-Solvent E	1 l
34811	HYDRANAL®-Titrant 2	To use with HYDRANAL®-Solvent or HYDRANAL®-Solvent E	500 ml; 1 l; 2.5 l
34730	HYDRANAL®-Solvent E	Methanol free solvent to use with HYDRANAL®-Titrant or HYDRANAL®-Titrant E	1 l; 2.5 l; 500 ml
34800	HYDRANAL®-Solvent	To use with HYDRANAL®-Titrant E or HYDRANAL®-Titrant	1 l; 2.5 l
34812	HYDRANAL®-Solvent CM	To use with HYDRANAL®-Titrant for titration of fats and oils	1 l; 2.5 l
34749	HYDRANAL®-Solvent Oil	To use with HYDRANAL®-Titrant for titration of oils	1 l

### Coulometric Karl Fischer titration

Cat. No.	Product	Description	Pack Size
34726	HYDRANAL®-Coulomat E	Ethanol based reagent to use as anolyte and catholyte	500 ml
34807	HYDRANAL®-Coulomat A	Anolyte for cells with diaphragm, reagent contains chloroform	500 ml
34810	HYDRANAL®-Coulomat AD	Reagent for cells without diaphragm	500 ml
34829	HYDRANAL®-Coulomat AF-7	Anolyte suitable for coulometer AF 7	1 l
34836	HYDRANAL®-Coulomat AG	Anolyte suitable for cells with and without diaphragm	500 ml; 1 l
34843	HYDRANAL®-Coulomat AG-H	Anolyte for titration of long-chained hydrocarbons (free of halogenated hydrocarbons)	500 ml
34739	HYDRANAL®-Coulomat AG	Oven Anolyte for determination with a KF oven	500 ml
34820	HYDRANAL®-Coulomat AK	Anolyte for titration of ketones	500 ml
34840	HYDRANAL®-Coulomat CG	Catholyte, free of halogenated hydrocarbons	25 ml; 50 ml
34821	HYDRANAL®-Coulomat CG-K	Catholyte for titration of ketones	50 ml

## Product Range of HYDRANAL®-Reagents

### Standards for Karl Fischer titration

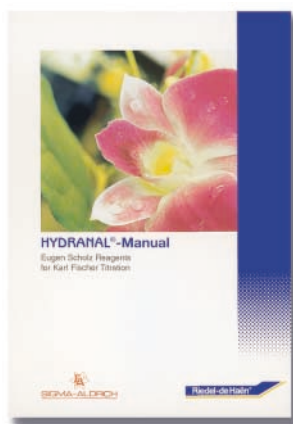
Cat. No.	Product	Description	Pack Size
34847	HYDRANAL®-Water Standard 0.10	Standard for coulometric KF titration, 1 g contains 0.10 mg = 0.01% water at 20 °C	40 ml
34828	HYDRANAL®-Water Standard 1.00	Standard for coulometric KF titration, 1 g (1 ml) contains 1.00 mg = 0.10 % water at 20 °C	40 ml
34849	HYDRANAL®-Water Standard 10.0	Standard for volumetric KF titration, 1 g (1 ml) contains 10.0 mg = 1.00% water at 20 °C	80 ml
34748	HYDRANAL®-Water Standard KF-Oven	Solid standard for control of KF ovens, assay of water: 5.55 ± 0.05%	10 g
34802	HYDRANAL®-Water-in-methanol Standard 5.00	Standard for volumetric back titration, water content: 5.00 ± 0.02 mg/ml	1 l
34813	HYDRANAL®-Standard 5.00	Non hygroscopic standard for volumetric KF titration	500 ml; 100 ml
34803	HYDRANAL®-Standard-sodium tartrate-2-hydrate	Primary standard for volumetric KF titration, assay of water: 15.66 ± 0.05%	100 g

### Auxillaries for Karl Fischer titration

Cat. No.	Product	Description	Pack Size
34804	HYDRANAL®-Buffer Acid	Buffer capacity: 5 mmol acid / ml	500 ml
37859	HYDRANAL®-Buffer Base	Buffer capacity: 1 mmol base / ml	500 ml; 1 l
34741	HYDRANAL®-Methanol dry	Solvent	1 l; 2.5 l
34724	HYDRANAL®-Formamide dry	Solubilizer	1 l
37863	HYDRANAL®-Chloroform	Solvent	1 l
37866	HYDRANAL®-Xylene	Solubilizer	1 l
37862	HYDRANAL®-Benzoic acid	Buffer substance	500 g
37865	HYDRANAL®-Salicylic acid	Buffer substance	500 g
37864	HYDRANAL®-Imidazole	Buffer substance	500 g
34788	HYDRANAL®-Humidity Absorber	Drying agent for air and gases	500 g; 1 kg

### Test kit for the visual water determination according to Karl Fischer without titrator

Cat. No.	Product	Description	Pack Size
37858	HYDRANAL®-Moisture Testkit	Testkit	1 piece
37857	HYDRANAL®-Titrant Component	Refill pack for HYDRANAL®-Moisture Testkit	100 ml



Please ask for your personal copy of our **HYDRANAL®-Manual**.

For technical help, please contact our Karl Fischer Help Lines:

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### HYDRANAL®-Technical Help

Karl Fischer titration requires high performance reagents and instrumentation to obtain results with high accuracy. Specific theoretical knowledge and practical experience are also of high importance and, unfortunately, are not often found in college or industrial training programs. Additionally, existing applications or measurement protocols are frequently outdated since they were simply passed on over the years without the necessary revisions or changes. To provide analysts around the world with the most up-to-date and product-specific information, we have established a Karl Fischer help line in Germany and a **HYDRANAL®-Technical Center** in USA. Please, do not hesitate to contact our Karl Fischer help lines or the technical service at your local office.

**HYDRANAL® – over 20 years experience in Karl Fischer Titration**

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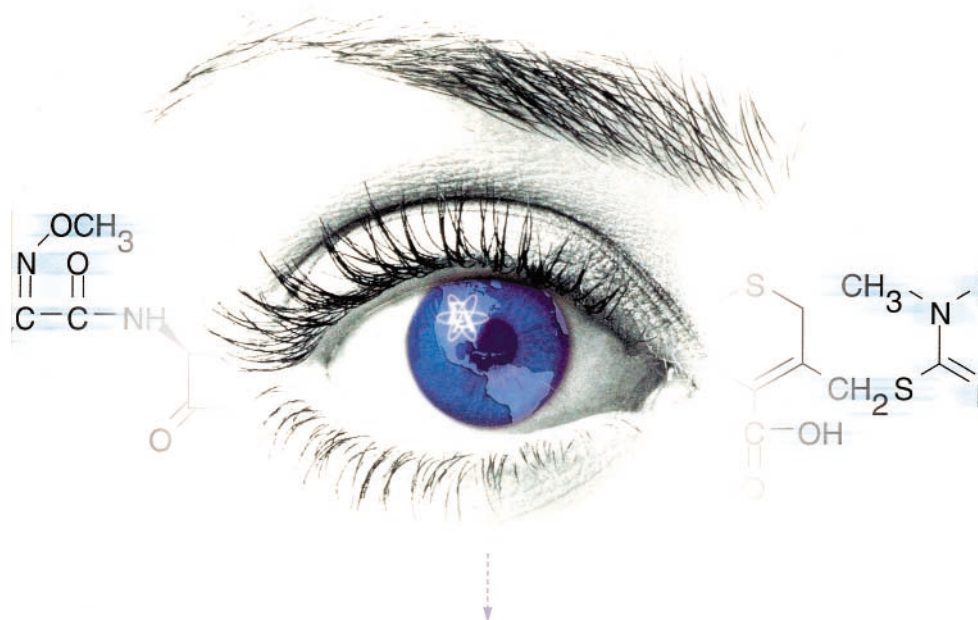
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