

# **HIGH CONFIDENCE. ACCURATE RESULTS.**

Hydranal™ Reagents for Water  
Determination by Karl Fischer Titration.



**Honeywell**

# HYDRANAL™ Reagents from Honeywell Research Chemicals

Water content can affect product quality, texture, shelf life, chemical stability and reactivity. Karl Fischer titration is a universally accepted method for measuring water content in all types of substances, including chemicals, oils, pharmaceuticals and food. In 1979, researcher Dr. Eugen Scholz improved Karl Fischer titration by replacing noxious pyridine with imidazole. This innovation became the foundation of Hydranal™, the world's leading pyridine-free reagents for Karl Fischer titration.

From Dr. E. Scholz's pioneering research to the ongoing product improvements of today, Honeywell offers a wide range of Karl Fischer reagents for both volumetric and coulometric titrations for nearly all types of samples, completed by a broad range of standards.

With the inclusion of Fluka™ into Honeywell Research Chemicals, Hydranal became an important part of the overall product portfolio. Hydranal reagents and water standards have always been developed and produced in our plant in Seelze, Germany, meaning you can be sure to enjoy the same composition, quality, service and technical support you always have.

**Honeywell is your partner for reliable and easy-to-use pyridine-free Karl Fischer reagents**

## Advantages of HYDRANAL Reagents:

- High titration speed
- Stable end points
- Accurate results
- Long shelf life
- Wide applicability
- World leading technical support

## HYDRANAL Product Line at a Glance

Product Line	Product Description
HYDRANAL-Composite	The most flexible and commonly used reagents for one-component volumetric titration
HYDRANAL Special Media	Special reagents like Methanol Rapid, E-Types and K-Types
HYDRANAL-Titrant/Solvent	Reagents for two-component volumetric titration
HYDRANAL-Coulomat	Reagents for coulometric titration for samples with low water content
HYDRANAL-Water Standards	Standards with verified water content for titer determination, monitoring precision, accuracy, validation and inspection of Karl Fischer titrators
HYDRANAL-CRM Water Standards	Certified Reference Materials for titer determination, monitoring precision, accuracy, validation and inspection of Karl Fischer titrators



# The Chemistry of Karl Fischer Titration

The Karl Fischer technique for water determination, invented in 1935 by Karl Fischer, is a titration based on the Bunsen reaction. In 1979 it was postulated by Dr. E. Scholz as a two-step equation:



*ROH = alcohol, typically methanol*

*R'N = base*

The oxidation of alkylsulfite to alkylsulfate in reaction (2) consumes water, which ideally comes only from the sample. Since water and iodine are consumed in a 1:1 stoichiometric ratio, the amount of water in the original sample is calculated by the amount of iodine required to complete the reaction. The iodine is measured either volumetrically directly by volume or coulometrically by the amount of current required for the generation of iodine.

## How the Base Affects Reaction Kinetics

The type of base (R'N) and its concentration affect the overall reaction rate. Traditionally, pyridine was used as the base. However, because of its weak basicity, pyridine cannot completely neutralize the alkyl-sulfurous acid intermediate. As a result, reaction (1) is slow, does not go to completion and the end point is not stable. Because of this lack of stability, the repeatability of the results is often very poor. In addition, pyridine has a noxious odor.

## Imidazole and 2-Methylimidazole as Alternatives to Pyridine

Dr. E. Scholz and his research team sought to replace the pyridine with a stronger base with a higher affinity for the alkylsulfite. Imidazole was found to have even more benefits than pyridine besides not having the noxious odor. Imidazole allows reaction (1) to go to completion rapidly and provides a stable end point. Later on researchers found that adding a second base, 2-methylimidazole, to the imidazole, enhances stability and reduces the appearance of undesired crystallization.



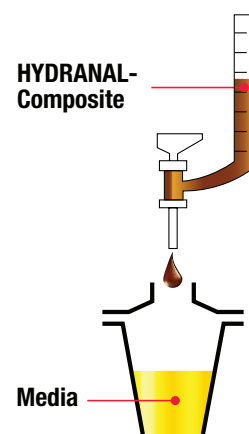
# Volumetric One-Component Titration - Titrating Agents

## HYDRANAL-Composite

Hydranal-Composite is the world's most frequently used pyridine-free Karl Fischer reagent. This one-component reagent has been proving its capabilities in volumetric titration for more than thirty five years in a large range of applications in the most diverse fields of research and industry. Ongoing development work has achieved significant improvements to this reagent.

### Advantages of HYDRANAL One-Component Reagents:

- Unlimited water capacity
- Convenient and easy to use
- The greatest flexibility in working media selection
- Suitable for methanol-reacting compounds, e.g. ketones and aldehydes
- Long shelf life (three years)



## Improved Composition

Hydranal-Composite contains all the reactants including iodine, sulfur dioxide, and the bases imidazole and 2-methylimidazole, dissolved in diethylene glycol monoethyl ether (DEGEE). Adding 2-methylimidazole in addition to imidazole improves the stability and eliminates the formation of crystals which can interfere with the titrator's performance. The crystallization of the reagent was occasionally observed under the influence of airborne moisture and also after prolonged residence of the reagent in the Karl Fischer titrator's tube system. This effect is prevented by a new and improved formulation.

## Enhancement of Titer Stability

When comparing the old and new formulation it becomes obvious that the new formulation is significantly more stable with a loss of concentration less than 5% per year vs. approx. 10% for the old formulation. Hydranal-Composite is additionally stabilized with DEGEE as a solvent. The results of the tests into titer decline are shown in Figure 1.

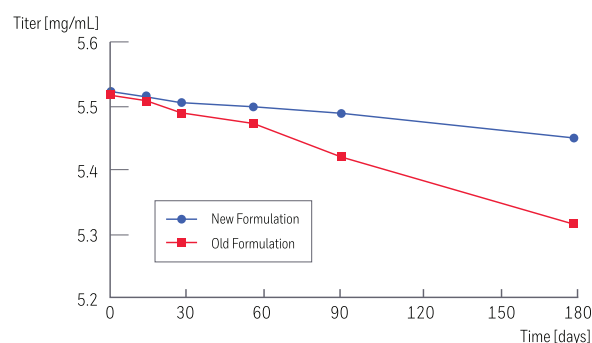


Figure 1. Results of the titer stability tests

Product Number	Product Name	Description	Packaging
34827	HYDRANAL-Composite 1	One-component reagent, titer ~1 mg/mL	500 mL; 1 L
34806	HYDRANAL-Composite 2	One-component reagent, titer ~2 mg/mL	500 mL; 1 L; 2.5 L
34805	HYDRANAL-Composite 5	One-component reagent, titer ~5 mg/mL	500 mL; 1 L; 2.5 L
34816	HYDRANAL-Composite 5 K	One-component reagent for titration of ketones and aldehydes, titer ~5 mg/mL	500 mL; 1 L; 2.5 L

# Volumetric One-Component Titration - Media

With one-component reagents the medium (i.e. the solvent required) is chosen according to the dissolution and chemical properties of the sample substance being analyzed. The most commonly used medium is dry methanol.

The speed, time taken and accuracy of the Karl Fischer reaction is influenced by the medium used in the titration vessel. The Hydranal-Composite, one-component reagents, are already buffered to an optimum of pH by using imidazoles. Thus the performance of the titrating agent is optimized to ensure a rapid Karl Fischer titration, however, there is still room for improvement on the use of the solvent.

## HYDRANAL-Methanol Rapid

Methanol is the most commonly used medium in the titration vessel, however it is an unbuffered solvent. When using Hydranal-Methanol Rapid, you will see a clear improvement in speed and accuracy of the titration. This is due to the accelerators in the medium, which are unique to Hydranal-Methanol Rapid and enable an optimal Karl Fischer titration (see Figure 2).

## HYDRANAL-CompoSolver E

In case a less toxic solvent is preferred, Hydranal-CompoSolver E, an ethanol based medium, has a similar performance to Hydranal-Methanol Rapid.

## HYDRANAL-Solver (premixed)

Many non-polar samples (e.g. oils, fats, organic components) appear with a poor solubility in methanol and require the addition of a solubilizer. To overcome these challenges, a series of specially designed media has been developed based on the most suitable solvent mix.

## HYDRANAL-K Media

For compounds reacting with methanol, like ketones and aldehydes, three different media have been developed. Comparing the three media based on their toxicity and capacity to suppress side effects, we recommend the use of Hydranal-Medium K as the first choice.

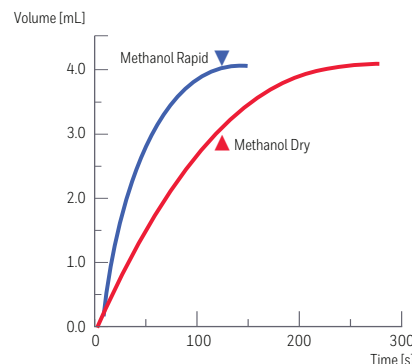


Figure 2. Titration of 20 mg water

## Advantages of HYDRANAL- Methanol Rapid:

- Much shorter titration time
- Rapid end point
- High accuracy of the analysis

Product Number	Product Name	Description	Packaging
37817	HYDRANAL-Methanol Rapid	Medium containing accelerators	1 L; 2.5 L
34741	HYDRANAL-Methanol Dry	Medium for general use	1 L; 2.5 L
34734	HYDRANAL-CompoSolver E	Ethanol-based medium containing accelerators	1 L; 2.5 L
34697	HYDRANAL-Solver (Crude) Oil	Working medium containing methanol, xylene and chloroform for titration in oils	1 L; 2.5 L
37855	HYDRANAL-LipoSolver CM	Working medium containing methanol and chloroform for titration in non-polar samples	1 L
37856	HYDRANAL-LipoSolver MH	Working medium containing methanol and 1-hexanol for titration in non-polar samples	1 L
34698	HYDRANAL-Medium K	Less toxic working medium containing chloroform for ketones and aldehydes	1 L
34738	HYDRANAL-KetoSolver	Working medium free of halogenated solvents for ketones and aldehydes	500 mL; 1 L
34817	HYDRANAL-Working Medium K	Working medium containing chloroform and 2-chloroethanol for ketones and aldehydes	1 L

# Volumetric Two-Component Titration

## HYDRANAL-Titrant / Solvent

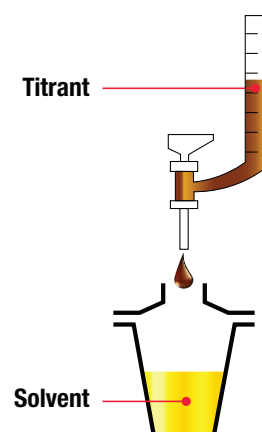
Two-component reagent have been developed to use the stability advantage of a pure alcoholic solution of iodine. Additionally, the buffered system provides a very fast titration performance.

### Composition

In two-component reagents the Karl Fischer reactants are separated into two solutions: the titrant and the solvent. Hydranal-Titrant contains iodine dissolved in an alcohol with a precisely defined concentration. Hydranal-Solvent is an alcoholic solution of sulfur dioxide and imidazole.

The alcohol is either methanol for standard reagents or ethanol for E-type reagents.

Further types of Solvent reagent based on different mixtures enable to meet the sample dissolution properties.



## Advantages of HYDRANAL Two-Component Reagents:

- High titration speed
- Ideal accuracy for small amounts of water
- High buffer capacity
- Exact and stable titer
- E-type reagents: reduced toxicity compared to methanol
- Long shelf life (three years for titrants, five years for solvents)

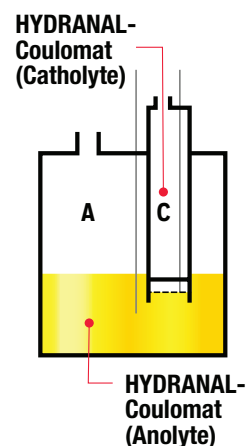
Product Number	Product Name	Description	Packaging
		<b>Methanol Based</b>	
34811	HYDRANAL-Titrant 2	Two-component reagent, titer ~2 mg/mL	500 mL; 1 L; 2.5 L
34801	HYDRANAL-Titrant 5	Two-component reagent, titer ~5 mg/mL	500 mL; 1 L; 2.5 L
34800	HYDRANAL-Solvent	Working medium for two-component titration	1 L; 2.5 L
		<b>Ethanol Based</b>	
34723	HYDRANAL-Titrant 2 E	Two-component reagent, titer ~2 mg/mL	1 L
34732	HYDRANAL-Titrant 5 E	Two-component reagent, titer ~5 mg/mL	500 mL; 1 L; 2.5 L
34730	HYDRANAL-Solvent E	Working medium for two-component titration	500 mL; 1 L; 2.5 L
		<b>Special Media</b>	
34812	HYDRANAL-Solvent CM	Working medium for two-component titration, containing methanol and chloroform for titration in non-polar samples	1 L; 2.5 L
34749	HYDRANAL-Solvent Oil	Working medium for two-component titration, containing methanol and 1-hexanol for titration in non-polar samples	1 L
34697	HYDRANAL-Solver (Crude) Oil	Working medium containing methanol, xylene and chloroform for titration in oils	1 L; 2.5 L

# Coulometric Titration

## HYDRANAL-Coulomat

Coulometric Karl Fischer titrations normally require two reagent solutions: an anolyte (the solution in the anodic compartment) and a catholyte (the solution in the cathodic compartment). Hydranal-Coulomat A-type or E-type reagents are used as anolytes. The anolytes contain iodide and a sulfur dioxide/imidazole buffer in suitable solvents. Hydranal-Coulomat CG reagents are used as catholytes.

Coulometric reagents based on different solvent compositions serve to support the broad variety of samples analyzed, i.e. Hydranal-Coulomat Oil contains methanol, xylene and chloroform for titration in oils or methanol-free Hydranal-Coulomat AK for titration of ketones to suppress negative side effects. Furthermore, some working techniques are supported by special reagents i.e. the use of Karl Fischer oven by Hydranal-Coulomat AG-Oven or the use of a cell without diaphragm by Hydranal-Coulomat AD.



## Coulometric Cells

There are two different types of coulometric cells: those with and those without a diaphragm. The diaphragm separates the anode chamber from the cathode chamber. Oxidation of  $I^-$  to  $I_2$  occurs at the anode, whereas the reduction of protons to  $H_2$  occurs at the cathode. For cells without a diaphragm the anodic and cathodic compartments are not separated and only one reagent, the anolyte, is needed. Though the latter coulometric cell may seem more convenient to use, the cell with diaphragm achieves the highest accuracy down to the trace range of water. Recommendation details are given in description below the table.

## Advantages of HYDRANAL Coulometric Reagents:

- Easy to use
- High accuracy for trace amounts of water
- Stable conditions of the titration vessel
- Broad product range
- Long shelf life (up to five years)

Product Number	Product Name	Description	Packaging
34807	HYDRANAL-Coulomat A	Anolyte preferred for cells with diaphragm*	500 mL
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, preferred for cells with diaphragm*	500 mL
34739	HYDRANAL-Coulomat AG-Oven	Anolyte for determination with Karl Fischer oven, suitable for cells with and without diaphragm	500 mL
34820	HYDRANAL-Coulomat AK	Anolyte for titration of ketones, preferred for cells with diaphragm*	500 mL
34868	HYDRANAL-Coulomat Oil	Anolyte for titration of oils, preferred for cells with diaphragm*	100 mL; 500 mL
34726	HYDRANAL-Coulomat E	Anolyte based on ethanol, suitable for cells with and without diaphragm	500 mL
34810	HYDRANAL-Coulomat AD	Anolyte preferred for cells without diaphragm	500 mL
34840	HYDRANAL-Coulomat CG	Catholyte	10 x 5 mL
34821	HYDRANAL-Coulomat CG-K	Catholyte for titration of ketones	10 x 5 mL

\* In theory all Hydranal-Coulomat anolytes may be used with either type of generator electrode: with or without a diaphragm. However, the anolytes which contain a co-solvent in addition to methanol show increased recoveries when used with a diaphragmless generator electrode. Therefore we recommend using a diaphragm generator electrode when working with a co-solvent containing anolyte. This will require the use of the appropriate catholyte.

# Titer Standardization and Instrument Inspection

## HYDRANAL-Water Standards

Quality management plays an important role in Karl Fischer titration. Calibration, validation and inspection of analytical instruments and reagents is performed with a specific amount of water, either pure water or water standards. The challenge with pure water is the low amount required (10–50 mg for volumetry, and 0.1–1 mg for coulometry), which is difficult to handle and weigh.

We therefore recommend Hydranal-Water Standards with an exactly confirmed water content for:

- Titer determination
- Monitoring precision and accuracy
- Validation and inspection of Karl Fischer titrators according to ISO, GMP, GLP and FDA guidelines

Traceability to a national standard or to a SI unit is often required in these guidelines. All Hydranal-Water Standards are tested against external reference material from national metrological institutions as the NIST (National Institute of Standards and Technology, USA) standard reference material SRM 2890, Water Saturated Octanol or CRM 4222 Water in Mesitylene from National Metrology Institute of Japan (NMIJ). Additionally, they are calibrated based on high purity water.

Liquid standards consist of a solvent mixture with specific composition and precisely determined water content. They are packaged in glass ampoules under argon. Each box contains ten single-use ampoules which are easy to open (pre-notched).

Solid standards contain defined amounts of chemically bound water suitable for both general use as well as for the Karl Fischer oven. These standards are packed in amber glass bottles.



## Advantages of HYDRANAL-Water Standards:

- Broad product range for volumetric and coulometric Karl Fischer applications
- Manufactured according to current ISO requirements
- Tested against NIST SRM 2890
- Long shelf life (up to five years)
- Convenient packaging
- Supplied with detailed instruction for use
- Report of Analysis showing the exact water content is included



## HYDRANAL-CRM Water Standards

Since 2014, Hydranal Center of Excellence in Seelze keeps its combined **ISO/IEC 17025** and **ISO 17034** accreditation. This is the highest achievable quality level for producers of Certified Reference Materials (CRMs). With the double accreditation, Hydranal introduced the very first commercially available CRM Water Standards for Karl Fischer titration.



Product Number	Product Name	Description	Packaging
34425	HYDRANAL-CRM Water Standard 10.0	Liquid CRM standard, water content 10.0 mg/g = 1.0%	10 x 8 mL
34426	HYDRANAL-CRM Water Standard 1.0	Liquid CRM standard, water content 1.0 mg/g = 0.1%	10 x 4 mL
34424	HYDRANAL-CRM Sodium Tartrate Dihydrate	Solid CRM standard, water content ~15.66%	10 g
34849	HYDRANAL-Water Standard 10.0	Liquid standard, water content 10.0 mg/g = 1.0%	10 x 8 mL
34828	HYDRANAL-Water Standard 1.0	Liquid standard, water content 1.0 mg/g = 0.1%	10 x 4 mL
34847	HYDRANAL-Water Standard 0.1	Liquid standard, water content 0.1 mg/g = 0.01% (shelf life 2 years, to be stored at 2-8°C)	10 x 4 mL
34446	HYDRANAL-Water Standard 0.1 PC	Liquid standard water content 0.1 mg/g = 0.01% (improved stability compared to 34847: shelf life 5 years, to be stored at room temp.)	10 x 4 mL
34694	HYDRANAL-Water Standard Oil	Liquid standard based on mineral oil, water content approx. 10 ppm (0.001%)	10 x 8 mL
34696	HYDRANAL-Standard Sodium Tartrate Dihydrate	Solid standard, water content ~15.66%	25 g
34693	HYDRANAL-Water Standard KF Oven 140-160°C	Solid standard for control of Karl Fischer ovens, water content ~5%, based on lactose	10 g
34748	HYDRANAL-Water Standard KF Oven 220-230°C	Solid standard for control of Karl Fischer ovens, water content ~5.55%, based on potassium citrate	10 g

# Auxiliaries for Karl Fischer Titration

Karl Fischer titration is applied to multifarious substances. The nuances in sample properties influence the Karl Fischer titration differently. There are a number of ways to adjust the working conditions.

## Solubilizers

In special cases the addition of solubilizer is required in order to enable a direct titration of the sample and avoid complicated and error-prone pre-dissolution and pre-extraction steps.

## Buffers

The Karl Fischer reaction is pH dependant, with pH 5-7.5 being the ideal range. Strongly acidic samples slow the reaction and must be neutralized without inducing an alkaline reaction of the working medium prior to starting the titration.

Strong bases can increase the pH of the working solution if the basicity exceeds the buffering capacity of the reagent.

A titration end point will not be reached. Strong bases also must be neutralized prior to starting the titration.

## Drying Agents

Special drying agents are suitable to hold the near environment of the Karl Fischer equipment on a low water level or to dry carrier gases in case of oven technique.

## HYDRANAL-Moisture Test Kit

For rough measurements without a titrator, special test kits for visual water determination according to Karl Fischer can be used. The set contains syringes, titration vessel and reagents: 2 x 500 mL Hydranal-Solvent E (34730), 100 mL Hydranal-Titrant 5 E (34732) and 100 mL Hydranal-Standard 5.0 (34813). Refills can be ordered separately.

Product Number	Product Name	Description	Packaging
34724	HYDRANAL-Formamide Dry	Solubilizer, max. 0.02% water	1 L
37863	HYDRANAL-Chloroform	Solubilizer, max. 0.01% water	1 L
37866	HYDRANAL-Xylene	Solubilizer, max. 0.02% water	1 L
34804	HYDRANAL-Buffer for Acids	Liquid buffer medium, based on imidazole	500 mL
37859	HYDRANAL-Buffer for Bases	Liquid buffer medium, based on salicylic acid	1 L
32035	HYDRANAL-Benzoic Acid	Buffer substance	500 g
37865	HYDRANAL-Salicylic Acid	Buffer substance	500 g
37864	HYDRANAL-Imidazole	Buffer substance	500 g
34813	HYDRANAL-Standard 5.0	Test solution for volumetric titration, water content 5.00 mg/mL	100 mL; 500 mL
34803	HYDRANAL-Sodium Tartrate Dihydrate	Test substance for volumetric titration, water content ~15.66%	100 g
34802	HYDRANAL-Water-in-Methanol 5.0	Reagent for volumetric back titration, water content 5.00 mg/mL	500 mL; 1 L
34788	HYDRANAL-Humidity Absorber	Drying agent for air and gases with indicator	500 g; 1 kg
34241	HYDRANAL-Molecular Sieve 0.3 nm	Drying agent for air and gases	250 g
37858	HYDRANAL-Moisture Test Kit	Test kit for the visual water determination according to Karl Fischer without titrator	1 kit

# Technical Support

For more than 40 years, the Hydranal Technical Service Team has been gathering extensive and unmet experience and insights into Karl Fischer titration and its related challenges.

If you are looking to improve your Karl Fischer titration performance, the team of Hydranal experts can support you with:

- Selecting the most suitable Karl Fischer reagents for your samples
- Recommending application methods
- Troubleshooting technical problems (solubility, side reactions, etc.)
- Technical Karl Fischer seminars and trainings
- Comprehensive literature

To learn more about Hydranal reagents, visit

<https://lab.honeywell.com/en/hydranal>



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Literature: <https://lab.honeywell.com/en/resources>

Laboratory Reports: <https://lab.honeywell.com/en/search/Hydranal-application-notes>

Events: <https://lab.honeywell.com/en/news-and-events>

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