

# HYDRANAL®

## Product Line Overview

**Fluka®**  
Analytical

Riedel-deHaën®



- Volumetric Titration with One-Component Reagents
- Volumetric Titration with Two-Component Reagents
- Coulometric Titration with HYDRANAL-Coulomat
- HYDRANAL-Water Standards
- HYDRANAL-E Types
- HYDRANAL Reagents for Ketones and Aldehydes
- Technical Support
- HYDRANAL Literature

## HYDRANAL Product Line Overview

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 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.

Since Dr. Scholz's pioneering research and with a spirit of ongoing product improvement, Sigma-Aldrich has launched a wide range of Karl Fischer reagents for both volumetric and coulometric titrations for nearly all types of samples.

**Sigma-Aldrich is a pioneer in the supply of safe, reliable and easy-to-use pyridine-free Karl Fischer reagents.**

### HYDRANAL Product Line at a Glance

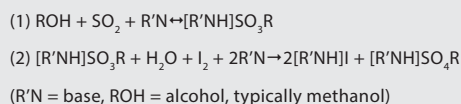
|                          |                                                                                                                                                             |
|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| HYDRANAL-Composite       | The most frequently used pyridine-free Karl Fischer reagent for one-component volumetric titration                                                          |
| HYDRANAL-Solvent/Titrant | Volumetric titration with two-component reagents for higher accuracy and stability                                                                          |
| HYDRANAL-Coulomat        | Coulometric titration for samples with low water contents                                                                                                   |
| HYDRANAL-Coulomat Oil    | Coulometric water determination in oils                                                                                                                     |
| HYDRANAL-Methanol Rapid  | Contains accelerants that speed up the reaction compared to pure methanol                                                                                   |
| HYDRANAL-K Types         | Specially designed reagents for determining water in ketones and aldehydes                                                                                  |
| HYDRANAL-E Types         | Reduced toxicity over methanol-containing reagents for both volumetric and coulometric titrations                                                           |
| HYDRANAL-Water Standards | Standards with a certified water content for titer determination, monitoring precision and accuracy and validation and inspection of Karl Fischer titrators |

### Advantages of HYDRANAL Reagents

- High speed titration
- Stable end points
- Accurate results
- No unpleasant odor
- Lower toxicity for increased safety and decreased environmental impact
- Long shelf life
- Wide applicability

### The Chemistry of Karl Fischer Titration

The Karl Fischer technique for water determination is a titration reaction based on the Bunsen equation:



The oxidation of alkylsulfite to alkylsulfate in reaction (2) consumes water, which should come only from the sample. Since water and iodine ( $\text{I}_2$ ) are consumed in a 1:1 stoichiometric ratio, the amount of water in the original sample is calculated by measuring the concentration of  $\text{I}_2$  remaining after the reaction is complete. The  $\text{I}_2$  is measured either volumetrically or coulometrically.

### How the Base Affects Reaction Kinetics

The type of base ( $\text{R}'\text{N}$ ) 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) does not go to completion, the reaction is slow 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. 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 all the benefits of pyridine, but without the noxious odor. As imidazole allows reaction (1) to go to completion, this is very rapid and the end point is very stable. Later on researchers at Sigma-Aldrich found that adding a second base, 2-methylimidazole, to the imidazole, enhances stability and reduces crystal formation.

## Volumetric Titration with One-Component Reagents HYDRANAL-Composite

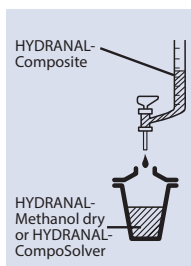
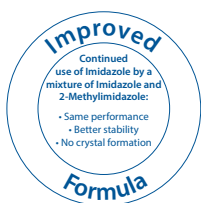


Figure 1 Volumetric one-component titration with HYDRANAL-Composite



### Advantages of one-component titration

- Unlimited water capacity
- Convenient and easy to use
- Long shelf life

### Composition

HYDRANAL-Composite is a one-component reagent for volumetric Karl Fischer titration. It contains all the reactants including iodine, sulfur dioxide, and the bases imidazole and 2-methylimidazole, dissolved in diethyleneglycol monoethyl ether (DEGEE). Using 2-methylimidazole in addition to imidazole improves the stability and eliminates the formation of crystals which can interfere with the titrators performance.

### Stability

HYDRANAL-Composite is stabilized with DEGEE. It improves stability; the concentration loss is less than 5% per year.

### Toxicity

HYDRANAL-Composites are free of pyridine and 2-methoxyethanol. DEGEE is non-hazardous.

### Using HYDRANAL-Composite

We recommend the following procedure for titrations with HYDRANAL-Composite (Figure 1):

1. Fill the burette with HYDRANAL-Composite
2. Add HYDRANAL-Methanol Rapid or HYDRANAL-Methanol dry or HYDRANAL-CompoSolver E into the titration vessel
3. Titrate the working medium to dryness with HYDRANAL-Composite
4. Add the sample
5. Titrate the water content with HYDRANAL-Composite

## Volumetric Titration with Two-Component Reagents HYDRANAL-Solvent/Titrant

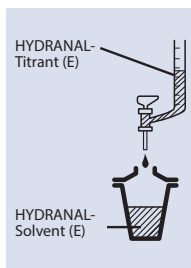


Figure 2 Volumetric two-component titration with HYDRANAL-Solvent (E)/Titrant (E)

### Advantages of two-component titration

- Higher titration speed
- Greater accuracy for small amounts of water
- Higher buffer capacity
- Exact and stable concentration

### Composition

Two-component reagents are separated in two solutions: the solvent and the titrant. HYDRANAL-Solvent is a solution of sulfur dioxide and imidazole in methanol.

HYDRANAL-Titrant contains a solution of iodine with a precisely defined concentration.

### Stability

The titrants have a shelf life of three years, the solvents five years, as long as the bottles are unopened.

### Toxicity

HYDRANAL-E-Type Reagents based on ethanol rather than methanol allow safer Karl Fischer titrations.

### Using HYDRANAL-Solvent/Titrants

We recommend the following procedure for the two-component titration technique (Figure 2):

1. Fill the burette with HYDRANAL-Titrant (E)
2. Add HYDRANAL-Solvent (E) to the titration vessel
3. Titrate the titration vessel to dryness with HYDRANAL-Titrant (E)
4. Add the sample
5. Titrate the water content with HYDRANAL-Titrant (E)

## Coulometric Titration

### HYDRANAL-Coulomat

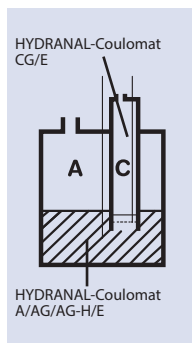


Figure 3 Coulometric titration with HYDRANAL-Coulomat reagents

#### Advantages of coulometric titration

- Easy to use
- Detects low concentrations of water
- High accuracy

#### Composition

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 reagents are used as anolyte. They contain iodide and a sulfur dioxide/imidazole buffer in suitable solvents. HYDRANAL-Coulomat CG reagents are used as catholytes. HYDRANAL-Coulomat E is used as both anolyte and catholyte. HYDRANAL-Coulomat E is based on ethanol.

#### Toxicity

All HYDRANAL-Coulomat reagents are free of toxic and noxious pyridine, carbon tetrachloride and 2-methoxyethanol. Methanol is a hazardous component, and it can be eliminated by using HYDRANAL-Coulomat E where ethanol replaces methanol.

#### Stability

If unopened, most HYDRANAL-Coulomat reagents have a shelf life of at least five years.

#### Using HYDRANAL-Coulomat Reagents

The following procedure is generally used for the coulometric determination of water (Figure 3):

1. Fill the cathodic compartment with HYDRANAL-Coulomat CG or E
2. Fill the anodic compartment with HYDRANAL-Coulomat A, AG, AG-H or E
3. Switch on the equipment and titrate
4. Push the analysis button
5. Inject the sample

#### Coulometry without a Diaphragm

Coulometric cells without diaphragm are available. They comprise only one compartment and require only one reagent. HYDRANAL-Coulomat E, AD, AG, AG-H, AG Oven and AK can be used with diaphragm-less cells. To use these reagents, follow the general procedure for coulometric determination of water except eliminate the catholyte solution.

## Titer Standardization

### HYDRANAL-Water Standards

Standards are necessary to check and control reagents, verify the reliability of titrations and to test instruments according to the requirements of ISO, GMP, GLP and FDA guidelines. The ISO standard requires that the "supplier shall control, calibrate ... (the) measuring and test equipment... to demonstrate conformance." Karl Fischer titrators are measuring or test instruments and therefore must be calibrated on a regular basis as part of an ongoing quality assurance program.

#### Advantages of HYDRANAL-Water Standards

- Packaged in glass ampoules under argon
- Convenient, single-use ampoules
- Long shelf life
- Manufactured according to current ISO standards
- Tested against NIST SRM 2890
- Supplied with detailed instructions and Certificate of Analysis

HYDRANAL-Water Standards are standards for volumetric or coulometric determinations (Figure 4). They are delivered with a Certificate of Analysis with the exact water content.

The liquid standards are packaged in glass ampoules under argon. Each box contains ten single-use ampoules. The shelf life is more than five years. HYDRANAL-Water Standard KF-Oven 220-230°C and HYDRANAL-Water Standard KF-Oven 140-160°C are solid standards for control of Karl Fischer ovens; they contain defined amounts of chemically combined water (exact value on CoA).



Figure 4 HYDRANAL-Water Standards for volumetric and coulometric Karl Fischer titration

## HYDRANAL-E Types

HYDRANAL-E reagents are an outcome of our ongoing objective to improve the safety and reduce environmental toxicity of our products. HYDRANAL-E reagents contain ethanol and permit reliable Karl Fischer titrations without toxic methanol. They represent the first less-toxic Karl-Fischer reagent line for both volumetric and coulometric titration.

### Advantages of HYDRANAL-E types

- Higher solubility for long-chained hydrocarbons
- Ketones like acetone can be titrated in HYDRANAL-CompoSolver E without side-reaction

- Shelf life and titer parameters comparable to methanol-containing reagents
- Can be used as anolyte and catholyte for coulometric cells with diaphragm

### HYDRANAL-E Products

- HYDRANAL-CompoSolver E, methanol free working medium used in conjunction with HYDRANAL-Composite
- HYDRANAL-Titrant 5 E, 2 E
- HYDRANAL-Solvent E
- HYDRANAL-Coulomat E

## HYDRANAL Reagents for Ketones and Aldehydes

Ketones and aldehydes interfere with conventional Karl Fischer titration because they react with methanol to form water, leading to incorrectly high water readings or vanishing end points. Simply replacing the methanol with 2-methoxyethanol does not give satisfying results. Side reactions are not suppressed and the Karl Fischer reaction rate is very slow. However, we found that certain other alcohols and glycolethers are good substitutes for methanol when determining water content of aldehydes and ketones.

### Volumetry: One-component titration

- HYDRANAL-Composite 5 K is the one-component reagent for the water determination in ketones and aldehydes. It contains iodine, sulfur dioxide, imidazole and 2-methylimidazole in DEGEE.
- HYDRANAL-Working Medium K is the corresponding solvent-system. It contains 2-chloroethanol and chloroform.

- HYDRANAL-Medium K is a perfect replacement for HYDRANAL-Working Medium K (free of 2-chloroethanol).
- HYDRANAL-KetoSolver is a working medium for volumetric water determination in ketones and aldehydes. It is used in conjunction with HYDRANAL-Composite 5 or HYDRANAL-Composite 5 K. It contains non-hazardous compounds and is biodegradable.

### Coulometry with Diaphragm

- HYDRANAL-Coulomat AK is a special anolyte solution for the analysis of ketones.
- HYDRANAL-Coulomat CG-K is the corresponding catholyte. It contains ammonium salts in an appropriate solvent.

### Coulometry without Diaphragm

- HYDRANAL-Coulomat AK can be used for the analysis of water in ketones in a diaphragm-less cell.

## Expert Technical Service

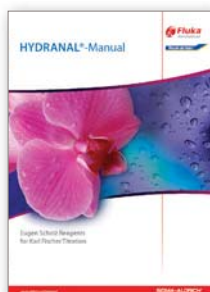
Take advantage of our expertise gained from over thirty years experience and our extensive applications database on Karl Fischer titration. Scientists in our HYDRANAL-Laboratory can suggest a solution to your analytical problem and, if necessary, develop an individual analytical method for you. Additional information can be found on our website:

[sigma-aldrich.com/hydranal](https://sigma-aldrich.com/hydranal)

### Our Technical Service includes:

- Help in solving technical problems (solubility, side reactions, etc.)
- Advice in selecting the appropriate Karl Fischer reagent
- Analysis of problematic samples
- Regular Karl Fischer workshops
- MSDS and Certificates of Analysis
- Comprehensive literature and applications for problematic samples

## Helpful HYDRANAL Literature and Contacts



### HYDRANAL Manual

A manual containing theory & practical advice on Karl Fischer Titration.

### HYDRANAL-Multimedia Guide CD

- Basics and techniques
- Video assisted introduction into the basics and investigation of samples
- Database with more than 850 Karl Fischer applications
- Complete product range
- 5 languages: German, English, Spanish, French, Chinese/Mandarin

For expert answers to all your KF questions, please contact our HYDRANAL specialists:

### For Europe and International

Thomas Wendt  
Technical Service HYDRANAL  
Tel.: +49-5137/8238-353  
Fax: +49-5137/8238-698  
E-mail: [hydranal@sial.com](mailto:hydranal@sial.com)

### For USA and Canada

Doug Clark  
HYDRANAL Technical Center  
Tel.: (800) 493-7262  
Fax: (314) 286-6699  
E-mail: [hydranal@sial.com](mailto:hydranal@sial.com)

**Table 1 Volumetric Karl Fischer titration – One-component reagents**

| Cat. No. | Product                     | Description                                                                                                     |
|----------|-----------------------------|-----------------------------------------------------------------------------------------------------------------|
| 34827    | HYDRANAL-Composite 1        | Reagent for volumetric one-component KF titration (methanol free), titer 0.8-1.2 mg/mL                          |
| 34806    | HYDRANAL-Composite 2        | Reagent for volumetric one-component KF titration (methanol free), titer 1.6-2.4 mg/mL                          |
| 34805    | HYDRANAL-Composite 5        | Reagent for volumetric one-component KF titration (methanol free), titer 4.5-5.5 mg/mL                          |
| 34816    | HYDRANAL-Composite 5K       | Reagent for volumetric one-component KF titration in aldehydes and ketones (methanol free), titer 4.5-5.5 mg/mL |
| 34734    | HYDRANAL-CompoSolver E      | Working medium for volumetric one-component KF titration (ethanol based)                                        |
| 34697    | HYDRANAL-Solver (Crude) Oil | Working medium for volumetric one- and two-component KF titration in oils                                       |
| 37855    | HYDRANAL-LipoSolver CM      | Working medium for volumetric one-component KF titration in non-polar substances, fats and oils                 |
| 37856    | HYDRANAL-LipoSolver MH      | Working medium for volumetric one-component KF titration in non-polar substances, fats and oils                 |
| 34738    | HYDRANAL-KetoSolver         | Working medium for volumetric one-component KF titration in aldehydes and ketones                               |
| 34698    | HYDRANAL-Medium K           | Working medium for volumetric one-component KF titration in aldehydes and ketones                               |
| 34817    | HYDRANAL-Working Medium K   | Working medium for volumetric one-component KF titration in aldehydes and ketones                               |
| 34741    | HYDRANAL-Methanol dry       | Working medium for volumetric one-component KF titration                                                        |
| 37817    | HYDRANAL-Methanol Rapid     | Working medium for fast volumetric one-component KF titration                                                   |

**Table 2 Volumetric Karl Fischer titration – Two-component reagents**

| Cat. No. | Product                     | Description                                                                                     |
|----------|-----------------------------|-------------------------------------------------------------------------------------------------|
| 34811    | HYDRANAL-Titrant 2          | Reagent for volumetric two-component KF titration, titer 1.98-2.02 mg/mL (20°C)                 |
| 34723    | HYDRANAL-Titrant 2 E        | Reagent for volumetric two-component KF titration (ethanol based), titer 1.96-2.04 mg/mL (20°C) |
| 34801    | HYDRANAL-Titrant 5          | Reagent for volumetric two-component KF titration, titer 4.95-5.05 mg/mL (20°C)                 |
| 34732    | HYDRANAL-Titrant 5 E        | Reagent for volumetric two-component KF titration (ethanol based), titer 4.95-5.05 mg/mL (20°C) |
| 34800    | HYDRANAL-Solvent            | Working medium for volumetric two-component KF titration                                        |
| 34730    | HYDRANAL-Solvent E          | Working medium for volumetric two-component KF titration (ethanol based)                        |
| 34812    | HYDRANAL-Solvent CM         | Working medium for volumetric two-component KF titration in non-polar substances, fats and oils |
| 34749    | HYDRANAL-Solvent Oil        | Working medium for volumetric two-component KF titration in non-polar substances, fats and oils |
| 34697    | HYDRANAL-Solver (Crude) Oil | Working medium for volumetric one- and two-component KF titration in oils                       |

**Table 3** Coulometric Karl Fischer titration

| Cat. No. | Product                   | Description                                                       |
|----------|---------------------------|-------------------------------------------------------------------|
| 34726    | HYDRANAL-Coulomat E       | Ethanol based reagent to be used as anolyte and catholyte         |
| 34807    | HYDRANAL-Coulomat A       | Anolyte preferred for cells with diaphragm                        |
| 34810    | HYDRANAL-Coulomat AD      | Reagent for cells without diaphragm                               |
| 34829    | HYDRANAL-Coulomat AF-7    | Anolyte suitable for coulometer AF 7                              |
| 34836    | HYDRANAL-Coulomat AG      | Anolyte suitable for cells with and without diaphragm             |
| 34843    | HYDRANAL-Coulomat AG-H    | Anolyte for titration of long-chained hydrocarbons                |
| 34739    | HYDRANAL-Coulomat AG Oven | Anolyte for determination with a KF oven                          |
| 34820    | HYDRANAL-Coulomat AK      | Anolyte for titration of ketones                                  |
| 34868    | HYDRANAL-Coulomat Oil     | Anolyte for titration of oils, preferred for cells with diaphragm |
| 34840    | HYDRANAL-Coulomat CG      | Catholyte (10 x 5 mL ampoules)                                    |
| 34821    | HYDRANAL-Coulomat CG-K    | Catholyte for titration of ketones (10 x 5 mL ampoules)           |

**Table 4** Test kit for the visual water determination according to Karl Fischer without titrator

| Cat. No. | Product                   | Description |
|----------|---------------------------|-------------|
| 37858    | HYDRANAL-Moisture Testkit | Testkit     |

**Table 5** Water Standards for Karl Fischer titration

| Cat. No. | Product                                     | Description                                                                                                                                            |
|----------|---------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| 34813    | HYDRANAL-Standard 5.0                       | Standard for volumetric KF titration 5.00 ± 0.02 mg/mL water                                                                                           |
| 34696    | HYDRANAL-Standard-sodium tartrate-dihydrate | Solid standard for volumetric KF titration, water content ~15.6%, exact value on CoA                                                                   |
| 34803    | HYDRANAL-Standard-sodium tartrate-dihydrate | Solid standard for volumetric KF titration, water content 15.66 ± 0.05 %                                                                               |
| 34802    | HYDRANAL-Water-in-methanol 5.0              | Reagent for volumetric back titration, water content: 5.00 ± 0.02 mg/mL                                                                                |
| 34847    | HYDRANAL-Water Standard 0.1                 | Standard for coulometric KF titration, 1 g contains 0.1 mg = 0.01 % water, 10 glass ampoules of 4 mL, tested against NIST SRM 2890. Exact value on CoA |
| 34828    | HYDRANAL-Water Standard 1.0                 | Standard for coulometric KF titration, 1 g contains 1.0 mg = 0.1 % water, 10 glass ampoules of 4 mL, tested against NIST SRM 2890. Exact value on CoA  |
| 34849    | HYDRANAL-Water Standard 10.0                | Standard for volumetric KF titration, 1 g contains 10.0 mg = 1.0 % water, 10 glass ampoules of 8 mL, tested against NIST SRM 2890. Exact value on CoA  |
| 34748    | HYDRANAL -Water Standard KF-Oven 220-230°C  | Solid standard for control of KF ovens, water content ~5.55 %, exact value on CoA                                                                      |
| 34693    | HYDRANAL-Water Standard KF-Oven 140-160°C   | Solid standard for control of KF ovens, water content ~5 %, exact value on CoA                                                                         |
| 34694    | HYDRANAL-Water Standard Oil                 | Standard for coulometric KF titration in oils, contains 10 glass ampoules of 8 mL. Tested against NIST SRM 2890. Exact value on CoA                    |

**Table 6** Auxiliaries for Karl Fischer titration

| Cat. No. | Product                        | Description                                            |
|----------|--------------------------------|--------------------------------------------------------|
| 32035    | HYDRANAL-Benzoic acid          | Buffer substance for KF titration                      |
| 37865    | HYDRANAL-Salicylic acid        | Buffer substance for KF titration                      |
| 37864    | HYDRANAL-Imidazole             | Buffer substance for KF titration                      |
| 34804    | HYDRANAL-Buffer Acid           | Liquid buffer medium for KF titration                  |
| 37859    | HYDRANAL-Buffer Base           | Liquid buffer medium for KF titration                  |
| 37863    | HYDRANAL-Chloroform            | Solubilizer, max. 0.01 % water                         |
| 37866    | HYDRANAL-Xylene                | Solubilizer, max. 0.01 % water                         |
| 34724    | HYDRANAL-Formamide dry         | Solubilizer, max. 0.02 % water                         |
| 34788    | HYDRANAL-Humidity Absorber     | Drying agent for air and gases                         |
| 34241    | HYDRANAL-Molecular Sieve 0.3nm | Molecular sieve suitable for Karl Fischer applications |