

Analytix^{Notes}

 **Fluka**

Riedel-deHaën®

HYDRANAL[®] Product Line Overview

HYDRANAL[®] Product Line

Volumetric Titration
**with One-Component
Reagents**

Volumetric Titration
**with Two-Component
Reagents**

Coulometric Titration
HYDRANAL[®]-Coulomat

HYDRANAL[®]-Water
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**for Ketones and
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SIGMA-ALDRICH

HYDRANAL® Product Line Overview Innovative Improvements to Karl Fischer Titration

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.

Table HYDRANAL® Product Line at a Glance

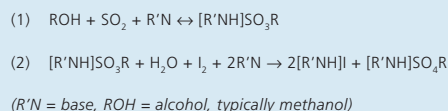
HYDRANAL®-Composite	The most frequently used pyridine-free Karl Fischer reagent for one-component volumetric titration
HYDRANAL®-Solvent/Titrant	Volumetric titration with two-component reagents for higher accuracy and stability
HYDRANAL®-Coulomat	Coulometric titration for samples with low water contents
HYDRANAL®-Coulomat Oil	Coulometric water determination in oils
HYDRANAL®-Methanol Rapid	Contains accelerants that speed up the reaction compared to methanol alone
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 titre 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 (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 I_2 remaining after the reaction is complete. The 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 alkylsulfurous 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

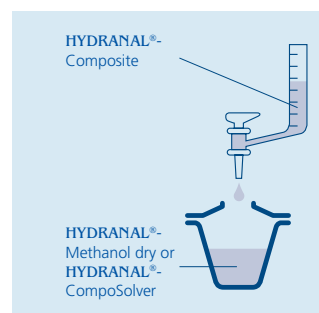
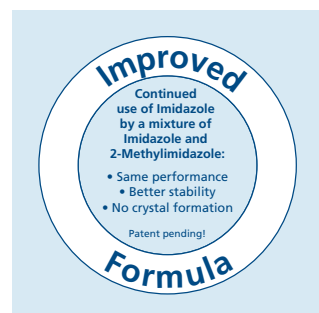


Figure 1 Volumetric one-component titration with HYDRANAL®-Composite



Advantages of one-component titration

- Unlimited range of water concentration
- 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 crystal which can interfere with titrators performance. For this new development we have applied for a patent.

Stability

HYDRANAL®-Composite is stabilized with DEGEE rather than 2-methoxyethanol (2-ME). DEGEE 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 unlike 2-ME which is fetotoxic and teratogenic (see ECETOC Technical Report No. 17).

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

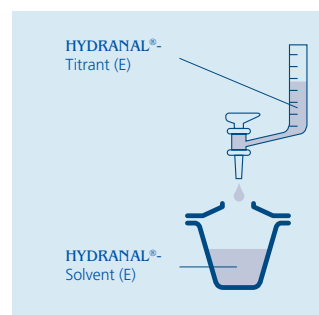


Figure 2 Volumetric two-component titration with HYDRANAL®-Solvent (E)/Titrant (E)

Advantages of two-component titration

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

Composition

With two-component reagents, the reactants are in two separate 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

Non-toxic 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

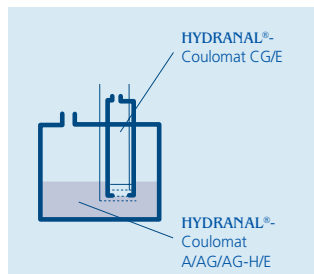


Figure 3 Coulometric titration with HYDRANAL®-Coulomat reagents

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 sulphur dioxide/imidazole buffer in suitable solvents. HYDRANAL®-Coulomat CG reagents are used as catholytes. HYDRANAL®-Coulomat E is used as both anolyte and catholyte. The non-toxic HYDRANAL®-Coulomat E is based on ethanol and does not require hazardous labeling.

Toxicity

All HYDRANAL®-Coulomat reagents are free of toxic and noxious compounds, such as pyridine, carbon tetrachloride and 2-methoxyethanol. Methanol is the most 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 the cell to dryness
4. Push the analysis button
5. Inject the sample

Coulometry without a Diaphragm

Some titration cells do not have a diaphragm. 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 unnecessary catholyte solution.

HYDRANAL®-Water Standards for volumetric and coulometric determinations



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

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 giving the actual 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 230 °C and HYDRANAL®-Water Standard KF-Oven 140-160 °C are solid Standards for control of Karl Fischer ovens; they contain certain amounts of chemically combined water (exact value on CoA).

Non-Toxic 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 non-toxic Karl-Fischer reagent line for both volumetric and coulometric titration.

Advantages of non-toxic HYDRANAL®-E types

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

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

Some 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

Special 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 glycol ethers 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, sulphur dioxide, imidazole and 2-methylimidazole in DEGE.
- HYDRANAL®-Working Medium K is the corresponding solvent-system. It contains chloroethanol and chloroform.

- HYDRANAL®-Medium K is a perfect replacement for HYDRANAL®-Working Medium K. It does not contain 2-chloroethanol and is therefore non toxic.
- 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 Support

Take advantage of our expertise gained from over twenty-five 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 at our website:

www.sigma-aldrich.com/hydranal

Our Total Technical Support includes:

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

Helpful HYDRANAL® Literature and Contacts

HYDRANAL® Manual

A 128-page manual containing theory & practical advice on Karl Fischer Titration

HYDRANAL®-Multimedia Guide CD

This Guide covers nine different subjects, and features a video-assisted description of volumetric and coulometric titration and a complete product listing. Over 500 applications and 500 laboratory reports on specific samples, detailed instructions designed according to ISO 9000, comparative analyses with pyridine-containing reagents and advice on disposal of spent reagents are included.

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

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Table 1 Volumetric Karl Fischer titration – One-component reagents

Cat. No.	Product	Description	Pack Size
34827	HYDRANAL®-Composite 1	One component reagent, titer: 1 mL ~ 1 mg water	500 mL, 1 L
34806	HYDRANAL®-Composite 2	One component reagent, titer: 1 mL ~ 2 mg water	500 mL, 1 L, 2.5 L
34805	HYDRANAL®-Composite 5	One component reagent, titer: 1 mL ~ 5 mg water	500 mL, 1 L, 2.5 L, 5 L
34816	HYDRANAL®-Composite 5K	One component reagent for titration of aldehydes and ketones, Titer: 1 mL ~ 5 mg water	500 mL, 1 L, 2.5 L
34734	HYDRANAL®-CompoSolver E	Methanol-free working medium	1 L, 2.5 L
34697	HYDRANAL®-Solver (Crude) Oil	To use with HYDRANAL®-Composite for titration of oils	1 L, 2.5 L
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
34738	HYDRANAL®-KetoSolver	To use with HYDRANAL®-Composite 5 K for titration of aldehydes and ketones	500 mL, 1 L
34698	HYDRANAL®-Medium K	To use with HYDRANAL®-Composite 5 K for titration of aldehydes and ketones	1 L
34817	HYDRANAL®-Working Medium K	To use with HYDRANAL®-Composite 5 K for titration of aldehydes and ketones	1 L
34741	HYDRANAL®-Methanol dry	Solvent, max. 0.01 % water	1 L, 2.5 L
37817	HYDRANAL®-Methanol Rapid	Solvent for a fast Karl-Fischer titration, max. 0.02% water	1 L, 2.5 L

Table 2 Volumetric Karl Fischer titration – Two-component reagents

Cat. No.	Product	Description	Pack Size
34811	HYDRANAL®-Titrant 2	To use with HYDRANAL®-Solvent E or HYDRANAL®-Solvent Titer: 1 mL = 2.00 ± 0.02 mg water (20°C)	500 mL, 1 L, 2.5 L
34723	HYDRANAL®-Titrant 2 E	Methanol free titrant to use with HYDRANAL®-Solvent E or HYDRANAL®-Solvent Titer: 1 mL = 2.00 ± 0.02 mg water (20°C)	1 L
34801	HYDRANAL®-Titrant 5	To use with HYDRANAL®-Solvent E or HYDRANAL®-Solvent Titer: 1 mL = 5.00 ± 0.02 mg water (20°C)	500 mL, 1 L, 2.5 L
34732	HYDRANAL®-Titrant 5 E	Methanol-free titrant to use with HYDRANAL®-Solvent E or HYDRANAL®-Solvent Titer: 1 mL = 5.00 ± 0.02 mg water (20°C)	500 mL, 1 L, 2.5 L
34800	HYDRANAL®-Solvent	To use with HYDRANAL®-Titrant E or HYDRANAL®-Titrant	1 L, 2.5 L
34730	HYDRANAL®-Solvent E	Methanol-free solvent to use with HYDRANAL®-Titrant E or HYDRANAL®-Titrant	500 mL, 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

Table 3 Coulometric Karl Fischer titration

Cat. No.	Product	Description	Pack Size
34726	HYDRANAL®-Coulomat E	Ethanol based reagent to be used 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
34868	HYDRANAL®-Coulomat Oil	Anolyte for titration of oils	100 mL, 500 mL
34840	HYDRANAL®-Coulomat CG	Catholyte, free of halogenated hydrocarbons 25 mL bottle resp. 10 x 5 mL ampoules	25 mL, 50 mL
34821	HYDRANAL®-Coulomat CG-K	Catholyte for titration of ketones contains 10 ampoules of 5mL	50 mL

Table 4 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

Table 5 Standards for Karl Fischer titration

Cat. No.	Product	Description	Pack Size
34813	HYDRANAL®-Standard 5.00	Non hygroscopic standard for volumetric Karl Fischer titration	100 mL, 500 mL
34696 	HYDRANAL®-Standard-sodium tartrate-dihydrate	Primary Standard for volumetric KF-titration Water content indicated on Certificate of Analysis Tested against NIST SRM 2890	25 g
34803	HYDRANAL®-Standard-sodium tartrate-dihydrate	Standard for volumetric Karl Fischer titration assay of water: 15.66 ± 0.05 %	25 g, 100 g
34802	HYDRANAL®-Water-in-methanol Standard 5.00	Standard for volumetric back titration, water content: 5.00 ± 0.02 mg/mL	1 L
34847	HYDRANAL®-Water Standard 0.10	Standard for coulometric Karl Fischer titration 1 g contains 0.10 mg = 0.01 % water contains 10 glass ampoules of 4 mL Tested against NIST SRM 2890	40 mL
34828	HYDRANAL®-Water Standard 1.00	Standard for coulometric Karl Fischer titration 1 g contains 1.00 mg = 0.10 % water contains 10 glass ampoules of 4 mL Tested against NIST SRM 2890	40 mL
34849	HYDRANAL®-Water Standard 10.0	Standard for volumetric Karl Fischer titration 1 g contains 10.0 mg = 1.00 % water contains 10 glass ampoules of 8 mL Tested against NIST SRM 2890	80 mL
34748	HYDRANAL®-Water Standard KF-Oven 230 °C	Solid standard for control of Karl Fischer ovens assay of water: 5.55 %	10 g
34693 	HYDRANAL®-Water Standard KF-Oven 140-160 °C	Solid standard for control of Karl Fischer ovens assay of water: 5.00 %	10 g

Table 6 Auxiliaries for Karl Fischer titration

Cat. No.	Product	Description	Pack Size
37862	HYDRANAL®-Benzoic acid	Buffer substance, max. 0.01 % water	500 g
34804	HYDRANAL®-Buffer Acid	Buffer capacity: 5 mmol acid/mL	500 mL
37859	HYDRANAL®-Buffer Base	Buffer substance, max. 0.03 % water	500 mL, 1 L
37863	HYDRANAL®-Chloroform	Solubilizer, max. 0.01 % water	1 L
34724	HYDRANAL®-Formamide dry	Solubilizer, max. 0.02 % water	1 L
37864	HYDRANAL®-Imidazole	Buffer substance, max. 0.1 % water	500 g
34788	HYDRANAL®-Humidity Absorber	Drying agent for air and gases	500 g, 1 kg
34241	HYDRANAL®-Molecular Sieve 0.3nm	Molecular sieve suitable for Karl Fischer applications	250g, 1kg
37865	HYDRANAL®-Salicylic acid	Buffer substance, max. 0.2 % water	500 g
37866	HYDRANAL®-Xylene	Solubilizer, max. 0.01 % water	1 L