

HYDRANAL® E-type reagents

Ethanol-based reagents for non-toxic Karl Fischer titrations

Helga Hoffmann, Technical Service HYDRANAL Manager helga.hoffmann@sial.com
Andrea Felgner, Product Manager Analytical Reagents andrea.felgner@sial.com



Karl Fischer titration is a universally accepted method for measuring water content in all types of substances, including chemicals, oils, pharmaceuticals and food. Sigma-Aldrich is a pioneer in the supply of safe, reliable and easy-to-use HYDRANAL Karl Fischer reagents. With the goal of improving laboratory safety and reducing toxicity, we offer HYDRANAL E-type reagents that permit reliable Karl Fischer titrations without toxic methanol.

Advantages and properties of HYDRANAL-E-type reagents:

- Reduced toxicity over methanol-containing reagents
- Better solubility of hydrophobic samples
- Additives increase reaction rate and conductivity of ethanol
- Several ketones can be titrated without side reactions
- Pyridine-free, like all HYDRANAL reagents
- Suitable for both volumetric and coulometric KF titrations
- Possible replacement for most methanolic KF methods
- Compatible with all titration equipment
- End-point color appears visually more intense compared to methanolic titrations
- Users fulfill requirements of DIN EN ISO 14001

Environmental responsibility and “green” chemistry

The chemical industry has responded to the need to reduce workers' exposure to hazardous and toxic substances, and to reduce and ultimately eliminate the release of these substances into our communities and environment. Because Karl Fischer titration is so prevalent across many industries worldwide, improving its safety can have a dramatic positive impact on industrial hygiene and the environment.

From the very inception of the line, all HYDRANAL reagents were designed to ensure reliable titrations that are free of noxious pyridine by replacing it with safe and odorless imidazole or diethanolamine. In a second significant improvement, Sigma-Aldrich researchers successfully replaced toxic methanol with

ethanol, thereby forming our HYDRANAL-E-types product line. By using ethanol, we have also been able to eliminate the need for halogenated hydrocarbons, like chloroform, dichloromethane and carbon tetrachloride as solubilizing agents.

Replacement of methanol in Karl Fischer titrations

Historically, ethanol was avoided in Karl Fischer reagents for two important reasons: very slow KF reaction rates and low conductivity in ethanol. HYDRANAL E-reagents solve these problems by incorporating accelerators to increase reaction rates and by using the most suitable additives to obtain conductivity comparable to methanol-containing reagents. As a result of these research efforts, our E-type reagents are now newly patent protected (by EP 0 933 634).

HYDRANAL E-type applications

The vast number of sample-specific procedures for Karl Fischer titration makes it impossible to name all advantages and disadvantages for every situation. During the development of the HYDRANAL E-product line, we analyzed samples from a large range of chemical groups and tested them for accuracy and extraction efficiency. We found that most applications that use methanol-based reagents are readily transferable to ethanol-based HYDRANAL reagents without difficulty.

Benefit of HYDRANAL E-types for hydrophobic samples

Besides having reduced toxicity, HYDRANAL E-reagents provide improved solubility of long-chained hydrocarbons compared to methanol-containing reagents. For example, only 4 mL of isooctane dissolve in methanol-based reagents, whereas 18 mL dissolve in HYDRANAL Solvent E and over 30 mL in HYDRANAL CompoSolver E. As a result, more analyses can be carried out in one charge of working medium. The addition of a solubilizing agent, like chloroform, is almost entirely unnecessary. However, if ethanol is not sufficient, solubilizing agents such as formamide, chloroform or xylene can be added to the HYDRANAL E-type working medium. Also, the temperature of the titration can be increased up to 50°C in order to improve sample solubility.

Table 1 Possible combinations of HYDRANAL E-type reagents for non-toxic Karl Fischer determinations

Volumetric one-component technique

Titration agent: HYDRANAL Composite 1 / 2 / 5

Working medium: HYDRANAL CompoSolver E

Volumetric two-component technique

Titration agent: HYDRANAL Titrant 2 E / 5 E

Working medium: HYDRANAL Solvent E

Coulometric technique

Anolyte: HYDRANAL Coulomat E

Catholyte: HYDRANAL Coulomat E

Composition of HYDRANAL E-type reagents

HYDRANAL Titrant 2 E and HYDRANAL Titrant 5 E are two-component titration reagents based on ethanol and iodine. They can be used with HYDRANAL Solvent or HYDRANAL Solvent E.

HYDRANAL Solvent E contains imidazole and diethanolamine as bases, as well as sulfur dioxide and ethanol.

HYDRANAL CompoSolver E contains ethanol as solvent and provides distinct advantages over methanol-based solvents, including: much shorter titration times than in pure methanol, suitability for water determination in ketones like acetone, and higher solubility for long-chained hydrocarbons.

HYDRANAL Coulomat E contains the bases imidazole and diethanolamine, as well as sulfur dioxide and ethanol. It can be used as both anolyte and catholyte for coulometric cells with and without diaphragm.

Reliable, precise and quantitative reference standards for titer determination

Sodium tartrate-2-hydrate is a common primary standard for volumetric KF titration. However, its solubility in ethanol is very limited. Therefore, when using HYDRANAL E-type reagents, we recommend using one of our HYDRANAL Water Standards for titer determination. HYDRANAL Water Standard 10.0 and HYDRANAL Standard 5.00 are specifically designed for volumetric KF determinations.

Applications

L510 Ethosuximide (3-Ethyl-3-methyl-2,5-pyrrolidinedione)

The sample is a waxy, solid mass, which is not easily homogenized. We recommend titration in HYDRANAL CompoSolver E, as the sample dissolves well in this ethanolic medium and titration times are very short (less than one minute). 30 mL HYDRANAL CompoSolver E are added to the titration vessel and pre-titrated with HYDRANAL Composite 5. About 2 g of the sample, exactly weighed using differential weighing, are added and the water content titrated with HYDRANAL Composite 5.

L514 Hydroxyzine pamoate

This substance is a fine powder, but it is insoluble in methanol. The sample was dissolved during titration in the non-toxic medium HYDRANAL CompoSolver E, titration duration less than 3 minutes. The sample also dissolved very quickly in the reagents of the two-component technique and titration was completed within 1–2 minutes. 30 mL HYDRANAL Solvent E / CompoSolver E are added to the titration vessel and pre-titrated with HYDRANAL Titrant 5 E / Composite 5. A 1 g sample is exactly weighed using differential weighing, and its water content titrated with HYDRANAL Titrant 5 E / Composite 5.

L537 Brake fluid

The tested brake fluid, consisting of glycol ether, borate ester and inhibitors, dissolved easily in the alcoholic media for Karl Fischer titration. 30 mL of HYDRANAL CompoSolver E / Solvent E is placed in the titration vessel and pre-titrated with HYDRANAL Composite 2 / Titrant 2 E. Approximately 5 g of the sample, determined by differential weighing, are added to the cell and the water content is titrated with HYDRANAL Composite 2 / Titrant 2 E. Using a coulometry cell with diaphragm, 5 mL of HYDRANAL Coulomat E are filled into the cathodic compartment and the anodic compartment is filled to the same level with HYDRANAL Coulomat E. For a coulometry cell without diaphragm, approximately 100 mL of HYDRANAL Coulomat E are added to the cell. The

cell automatically pre-titrates. When the drift is low and stable, 0.5–1 g of the sample, determined by differential weighing, are weighed precisely and injected into the cell using a syringe.

Table 2 HYDRANAL E-Type reagents and suitable water standards

Cat. No.	Brand	Description	Pack Size
34723	Riedel-de Haën	HYDRANAL Titrant 2 E (2.00 ± 0.02 mg H ₂ O / mL)	1 L
34732	Riedel-de Haën	HYDRANAL Titrant 5 E (5.00 ± 0.02 mg H ₂ O / mL)	500 mL, 1 L, 2.5 L
34730	Riedel-de Haën	HYDRANAL Solvent E	500 mL, 1 L, 2.5 L
34734	Riedel-de Haën	HYDRANAL CompoSolver E	1 L, 2.5 L
34726	Riedel-de Haën	HYDRANAL Coulomat E	500 mL
34813	Riedel-de Haën	HYDRANAL Standard 5.00 Water content 5.00 ± 0.02 mg/mL (20°C)	100 mL, 500 mL
34849	Riedel-de Haën	HYDRANAL Water Standard 10.0; Box contains 10 ampoules of 8 mL each Water content 10.00 mg/g; CoA included in each box; tested against NIST SRM 2890	80 mL

Contact us for expert technical assistance

Take advantage of our expertise gained from over twenty-five year experience and our extensive applications database on Karl Fischer titration. We 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: www.sigma-aldrich.com/hydranal.

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

Europe and the rest of the world (Except USA and Canada):

Ms Helga Hoffmann
Technical Service HYDRANAL
Tel.: ++49-5137/8238-353
Fax: ++49-5137/8238-698
E-mail: helga.hoffmann@sial.com

USA and Canada:

Mr Doug Clark
HYDRANAL Technical Center
545 S. Ewing Ave
St. Louis, MO 63103, USA

Toll free: ++1-800-493-7262 (USA and Canada)

Fax: ++1-314-286-6699
E-mail: doug.clark@sial.com