



HYDRANAL[®]-E Types

The new dimension in non-toxic Karl Fischer titration

Moisture content can affect product quality, shelf life, chemical stability and reactivity. Karl Fischer titration is an 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 Karl Fischer reagents. Now, with the goal of improving laboratory safety and reducing environment toxicity, we offer HYDRANAL-E reagents that permit reliable Karl Fischer titrations without toxic methanol.

www.sigma-aldrich.com/hydranal

Ethanol-based reagents for non-toxic Karl Fischer titrations

The chemical industry has responded to the need to reduce exposure to toxic substances, and to reduce and ultimately eliminate the release of these substances into our environment. Because Karl Fischer titration is so ubiquitous, improving its safety can have a dramatic industrial and environmental impact. Sigma-Aldrich put its focus on increasing the safety of Karl Fischer titrations by targeting two chemicals in the reaction: the base and the alcohol. All HYDRANAL reagents already use safe, odorless imidazole or diethanolamine instead of the noxious pyridine originally used as a base. Next, research attention was turned to the alcohol, replacing the toxic methanol with ethanol in our HYDRANAL-E product line.

Methanol is the most commonly used alcohol. However, methanol is classified as poisonous according to chemical regulations. In order to reduce exposure and release of methanol, Sigma-Aldrich has developed a line of reagents, HYDRANAL-E reagents, that uses ethanol and therefore provides a methanol-free Karl Fischer titration. By using ethanol, also the use of ecologically questionable halogenated hydrocarbons, like chloroform, dichloromethane or carbon tetrachloride, can be avoided.

Historically, Karl Fischer titrations avoided ethanol for two important reasons. First, the reaction rate in pure ethanol is very slow compared to methanol. HYDRANAL-E reagents solve this problem by incorporating accelerators that increase the reaction rate in ethanol compared to methanol, thereby reducing the overall reaction time without interfering with the reaction or interpretation of the results. Second, the conductivity of ethanol is lower compared to methanol, which can result in a slower, more variable reading. To overcome this drawback, HYDRANAL-E reagents are formulated with the most suitable additives. As a result, the conductivity of HYDRANAL-E reagents is comparable to methanol-containing reagents. When carrying out volumetric KF titrations, an added benefit of ethanol is that the end-point color is more intense compared to a methanolic reagent. These improved formulations are patent-protected.

The vast number of sample-specific procedures for Karl Fischer titration makes it impossible to name all the 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 HYDRANAL-E reagents.

Benefit of HYDRANAL-E: Hydrophobic Samples – Longer alkyl chain length of ethanol gives HYDRANAL-E enhanced solubility and extraction efficiency toward hydrophobic samples.

Besides having reduced toxicity, the HYDRANAL-E reagents show improved solubility for long-chained hydrocarbons compared to methanol-containing reagents. For example, only 4 mL of iso-octane dissolve in methanol-based reagents, but 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 solubilizer, like chloroform, is typically not needed. However, if necessary, solubilizing agents such as formamide, chloroform or xylene can be added to the HYDRANAL-E working medium. Temperature of the titration can also be increased up to 50°C in order to improve sample solubility.

Benefit of HYDRANAL-E: Ketones

Water content of many ketones, including acetone, can be determined using HYDRANAL-CompoSolver E with HYDRANAL-Composite. Alcoholic side-reactions with ketones are often less pronounced in ethanol than in methanol.

34723 HYDRANAL-Titrant 2 E (titer 2.00 ± 0.02 mg H₂O/mL)

34732 HYDRANAL-Titrant 5 E (titer 5.00 ± 0.02 mg H₂O/mL)

34730 HYDRANAL-Solvent E

are two-component titration reagents containing ethanol and iodine. HYDRANAL-Titrants 2 E and 5 E can be used with other HYDRANAL reagents, for example HYDRANAL-Titrant 5 E with HYDRANAL-Solvent or HYDRANAL-Solvent E with HYDRANAL-Titrant. HYDRANAL-Solvent E is used as the working solvent in the titration vessel. It contains the bases imidazole and diethanolamine, as well as sulfur dioxide and ethanol.

34734 HYDRANAL-CompoSolver E

is a working medium for the standard one-component reagent HYDRANAL-Composite and contains ethanol as solvent. Applied with HYDRANAL-Composite, HYDRANAL-CompoSolver E enables a methanol-free analysis with a one-component reagent. HYDRANAL-CompoSolver E has distinct advantages over methanol-based solvents. For example, the titration time in HYDRANAL-CompoSolver E is much shorter than in pure methanol. Additionally, it can be used to determine water in ketones, like acetone, and has greater solubility toward long-chained hydrocarbons than methanol.

Titer determination

Sodium tartrate dihydrate as a common standard for KF titration shows very limited solubility in ethanol, therefore the use of liquid HYDRANAL Water standards is recommended.

HYDRANAL-Water Standard 10.0 and HYDRANAL-Standard 5.00 should be used; water can also be used when measured precisely.

Cat. No.	Brand	Description	Package Size
34723	Fluka	HYDRANAL-Titrant 2 E	1 L
34732	Fluka	HYDRANAL-Titrant 5 E	500 mL; 1 L; 2,5 L
34730	Fluka	HYDRANAL-Solvent E	500 mL; 1 L; 2,5 L
34734	Fluka	HYDRANAL-CompoSolver E	1 L; 2,5 L
34726	Fluka	HYDRANAL-Coulomat E	500 mL
34813	Fluka	HYDRANAL-Standard 5.00; Water content 5.00 ± 0.02 mg/mL (20°C) Water content 5.91 ± 0.02 mg/g	100 mL; 500 mL
34849	Fluka	HYDRANAL-Water Standard 10.0; Box contains 10 ampules of 8 mL each; Water content 10.00 mg/g, Certificate of Analysis included in each box Tested against NIST SRM 2890	80 mL

Some features of HYDRANAL-E-line include

- Reduced toxicity over methanol-containing reagents
- Pyridine-free like all HYDRANAL reagents
- For both volumetric and coulometric KF titrations
- Better solubility of hydrophobic samples
- Additives increase reaction rate and conductivity of ethanol
- Many ketones titrated without side-reaction
- End-point color appears visually more intense compared to methanol
- Replaces most methanolic methods
- Compatible with all titration equipment
- Fulfill the requirements of DIN EN ISO 14001

HYDRANAL E-type applications

The following table (see next page) presents the water content of some common solvents and chemicals determined using HYDRANAL-E reagents. 30 mL of either HYDRANAL-Solvent E or HYDRANAL-CompoSolver E were added to the titration vessel and titrated with HYDRANAL-Titrant 5 E or HYDRANAL-Composite 5, respectively. We tested the recovery rate of added water, the titration speed and the capacity of the working medium. Usually a total of 20 mL or 20 g of the substance under analysis was determined taking 10 mL or 10 g individual sample sizes for each titration. If a smaller total quantity was possible in one charge of working medium, the letter alongside explains the reason for the limitation. The water content of the samples we analyzed is given, but it is by no means a lower or upper limit.

Product Information

In addition to this LabInfo, a number of other brochures is available about HYDRANAL reagents, the HYDRANAL manual as well as the new HYDRANAL Multimedia Guide CD. Please request these items at our HYDRANAL laboratories.

www.sigma-aldrich.com/hydranal

Contact

USA and Canada

Mr. Doug Clark HYDRANAL®-Technical Center
Toll free: +1-800-493-7262 (USA and Canada)
Fax: +1-314-286-6699
E-Mail: doug.clark@sial.com

Europe and the Rest of the World

Ms. Helga Hoffmann, Technical Service HYDRANAL
Tel.: +49 (0) 5137 8238-353
Fax: +49 (0) 5137 8238-698
E-Mail: helga.hoffmann@sial.com

Table Classes of commonly used substances

Sample		Hydranal-E Reagent: Titrant 5 E / Solvent E	Hydranal-E Reagent: Composite 5 / CompoSolver E	Water content
Hydrocarbons	<i>n</i> -Hexane	20 mL	20 mL	0.004%
	Toluene	20 mL	20 mL	0.020%
	Xylene	20 mL	20 mL	0.011%
	Dodecane	1 mL (S)*	15 mL (S)*	0.005%
	1-Tetradecene	20 mL	20 mL	0.005%
	<i>iso</i> -Octane	20 mL	20 mL	0.004%
	Cyclohexane	20 mL	20 mL	0.002%
	Dicyclopentadiene	5 mL (P)*	20 mL	0.003%
	2,5-Norbornadiene	20 mL	20 mL	0.013%
	Halogenated hydrocarbons	Dichlormethane	20 mL	20 mL
1-Chlorooctane		20 mL	20 mL	0.016%
4-Chlortoluene		20 mL	20 mL	0.007%
1-Bromtetradecane		20 mL	20 mL	0.007%
Alcohols	1-Propanol	20 mL	20 mL	0.100%
	2-Propanol	20 mL	20 mL	0.000%
	1-Hexanol	20 mL	20 mL	0.020%
	1-Octanol	20 mL	20 mL	0.015%
Ketones	Acetone	not possible	10 mL (R)*	0.230%
	Methyl- <i>iso</i> -butyl ketone	1 mL (R)*	20 mL	0.032%
	3-Octanone	1 mL (R)*	10 mL (R)*	0.450%
	Cyclohexanone	not possible	2 mL (R)*	0.050%
	Acetophenone	2 mL (R)*	10 mL (R)*	0.019%
	Benzophenone	6 g (S)*	5 g (S)*	0.006%
	2-Pyrrolidone	5 mL (R)*	10 mL (R)*	0.091%
	N-Methylpyrrolidone	10 mL (R)*	10 mL (R)*	0.140%
Ethers	1,4-Dioxane	20 mL	20 mL	0.052%
	Polyethylene glycol	10 mL (I)*	5 mL (I)*	0.130%
	Anisole	20 mL	20 mL	0.022%
	1,3,5-Trioxane	1 g (S)*	1 g (S)*	0.007%
Carboxylic acids	Acetic acid	20 mL	20 mL	0.026%
	Propionic acid	20 mL	20 mL	0.047%
	2-Ethylhexanoic acid	20 mL	20 mL	0.094%
	Malonic acid	10 g (S)*	10 g (I)*	0.150%
	Benzoic acid	10 g (S)*	10 g (S)*	0.004%
	Salicylic acid	10 g (S)*	8 g (S)*	0.004%
	Dichloroacetic acid	4 mL (R)*	5 mL (R)*	0.019%
Amines	<i>n</i> -Propylamine	1 mL (A)*	2 mL (A)*	0.042%
	<i>n</i> -Butylamine	1 mL (A)*	2 mL (A)*	0.048%
	Diethanolamine	3 g (A)*	5 g (A)*	0.017%
	Triethanolamine	3 g (A)*	3 g (A)*	0.022%
	1,2-Diaminoethane	not possible	not possible	-
	Diethylentriamine	not possible	not possible	-
	Morpholine	2 g (A)*	2 g (A)*	0.011%
	Aniline	not possible	2 mL (A)*	0.011%
	N-Methylaniline	5 mL (R)*	20 mL	0.050%
	Pyridine	10 mL	20 mL	0.013%
	Imidazole	10 g	20 g	0.040%

* A = 5-7 g salicylic acid are added in order to neutralize basic amines, I = Indication, S = solubility, R = side-reaction, P = precipitation.

World Headquarters

3050 Spruce St., St. Louis, MO 63103
(314) 771-5765
sigma-aldrich.com

Order/Customer Service (800) 325-3010 • Fax (800) 325-5052

Technical Service (800) 325-5832 • sigma-aldrich.com/techservice

Development/Bulk Manufacturing Inquiries **SAFC**™ (800) 244-1173

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