

HYDRANAL® reagents for Karl Fischer titration of water in aldehydes and ketones

Reagents with performance and safety advantages for both volumetric and coulometric methods

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

Using the Karl Fischer (KF) titration method to determine water in aldehydes and ketones can be challenging. With conventional methanol or methanol-containing KF reagents, aldehydes and ketones can undergo nucleophilic addition reactions that lead to the formation of acetals or ketals and water (see **Figure 1**). The produced water leads to erroneously high results and vanishing end-points. Additionally, a second side reaction, the bisulphite addition, can occur during the titration of aldehydes. Some of the water in the sample, depending on the strength of its bonds, can be consumed by this reaction leading to erroneously low results (see **Figure 2**).

Figure 1 Aldehydes and ketones undergo nucleophilic addition of methanol resulting in formation of acetal or ketal and water

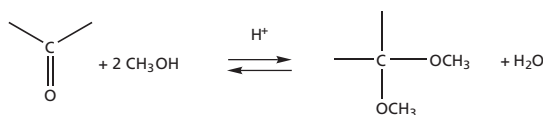
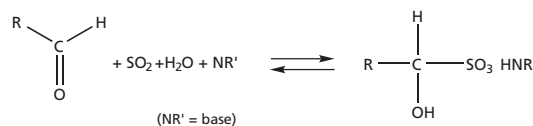


Figure 2 Bisulphite addition reaction consuming water



HYDRANAL K-reagents: Ideal for KF titration of aldehydes and ketones

Addressing this reactivity problem, researchers at Sigma-Aldrich found that certain halogenated alcohols (2-chloroethanol, trifluoroethanol) and 1-methoxy-2-propanol are particularly suitable for suppressing these side reactions. The methanol-free HYDRANAL K-reagents were developed based on these findings. HYDRANAL K-reagents prevent unwanted side reactions, eliminating or significantly reducing them as sources of error.

HYDRANAL Composite 5 K, designed for determination of water in aldehydes and ketones, consists of a solution of imidazole, sulphur dioxide and iodine in diethylene glycol monoethyl ether. We offer three different working media for HYDRANAL Composite 5 K: HYDRANAL KetoSolver, a halogen-free medium, HYDRANAL Medium K, a non-toxic medium and HYDRANAL Working Medium K, a medium that has excellent dissolving properties for difficult samples but contains chloroform and toxic 2-chloroethanol.

Elimination of nucleophilic addition by using a suitable working medium

The elimination of methanol in HYDRANAL KetoSolver, Medium K and Working Medium K presents a two-fold advantage. First, it eliminates unwanted side reactions like nucleophilic addition. Second, it improves the solubility of certain samples. For example, we found that as much as 5 g of 3-benzoylpropionic acid can be titrated in these media with suppression of ketal formation. In some cases, HYDRANAL Medium K can be used in conjunction with the standard volumetric reagent, HYDRANAL Composite 5.

Prevention of bisulphite addition by using HYDRANAL Composite 5 K

Adduct formation during bisulphite addition reactions consume water from the sample causing erroneously low results. This reaction can be avoided by using HYDRANAL Composite 5 K as titrating reagent in combination with HYDRANAL KetoSolver, Medium K or Working Medium K. Compared to HYDRANAL Composite 5, HYDRANAL Composite 5 K gives slightly slower reaction speed in order to maximise the suppression of the bisulphite addition.

The HYDRANAL reagents described above can also be used for the determination of water in substances other than aldehydes and ketones. HYDRANAL Medium K, Working Medium K and KetoSolver can act as a solvent for the determination of water in any substance where methanol can interfere with the titration and therefore must be avoided. Nearly universal in their applicability, they can also be used to titrate samples that do not present interference problems.

HYDRANAL Medium K: Non-toxic Karl Fischer reagent with performance and safety advantages

HYDRANAL Working Medium K is categorised as very toxic (T⁺) because it contains 2-chloroethanol. However, we have replaced toxic 2-chloroethanol with less hazardous alcohols in HYDRANAL Medium K, permitting its categorisation merely as harmful (X_n) due to its percentage of chloroform.

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Benefits of HYDRANAL Medium K over HYDRANAL Working Medium K

- Reduced toxicity for improved workplace safety while providing equal reactivity
- No water-producing side reactions
- No water-consuming side reactions when using HYDRANAL Composite 5 K as titrating reagent

HYDRANAL Medium K is a full-fledged substitute for HYDRANAL Working Medium K, providing the same sample capacity, speed and accuracy. It offers important application, safety and transportation benefits; because it is non-toxic, it not only improves workplace safety, it also reduces the amount of packaging material that is required and must be disposed of. In addition, HYDRANAL Medium K offers performance advantages with very reactive aldehydes such as propionaldehyde, butyraldehyde and crotonaldehyde. Capacity and accuracy are also improved for other compounds including salicylaldehyde, acetylacetone, 2,4-dihydroxyacetophenone and 2-benzolpyridine.

HYDRANAL KetoSolver: A halogen-free working medium

Our research into using different alcohols resulted in HYDRANAL KetoSolver, a working medium that is completely free of halogenated hydrocarbons. It can be used with both HYDRANAL Composite 5 or HYDRANAL Composite 5 K, depending on which is best for the sample. The main component of HYDRANAL KetoSolver is 1-methoxy-2-propanol, which suppresses the previously described side reactions, for the most part, and allows simple and reliable water determinations. Aldehydes and certain highly reactive ketones like cyclohexanone, trifluoroacetone and diacetyl require the use of HYDRANAL Composite 5 K as the titration agent.

Coulometric Karl Fischer titration in ketones

HYDRANAL Coulomat AK is an anolyte specially designed for the coulometric water determination in ketones. It contains imidazole, sulphur dioxide and iodide dissolved in a suitable solvent mixture and has a capacity of approximately 100 mg of water per 100 mL. HYDRANAL Coulomat AK can also be used as a single reagent for coulometry without diaphragm. HYDRANAL Coulomat CG-K is the corresponding catholyte. It does not contain halogenated hydrocarbons. The water capacity of 5 mL HYDRANAL Coulomat CG-K is 100 mg.

Recommendations for KF titration in aldehydes and ketones

Aldehydes

Short-chain aldehydes show a strong tendency to form acetals. Aromatic aldehydes tend to undergo the bisulphite addition. To overcome these potential interferences, we recommend using relatively small samples and titrating rapidly to suppress the formation of acetals and bisulphite compounds. Coulometry is not advised, but if it is necessary, the sample volume should be very small. For example, for water determination in aromatic aldehydes the sample volume must be less than 0.5 mL. Aliphatic aldehydes, like acetaldehyde, are highly reactive and tend to rapidly form acetals. Only volumetric titration with Methanol-free K-reagents is recommended and the amount of sample should be kept to a minimum.

Ketones

Ketones have a tendency to form ketals while at the same time forming water. Cyclohexanone and acetone react rapidly, while long-chain ketones and aromatic-substituted ketones show slower reaction rates. Reactive ketones are titrated with methanol-free K-reagents. The coulometric determination is possible by using HYDRANAL Coulomat AK and Coulomat CG-K reagents.

Table 1 Recommended procedures and reagents for Karl Fischer titration in selected aldehydes and ketones

Sample	Recommended KF procedure and respective HYDRANAL reagents		
	Volumetric 1-component technique (HYDRANAL Composite 5 K + HYDRANAL Medium K)	Coulometric technique with diaphragm (HYDRANAL Coulomat AK + HYDRANAL Coulomat CG-K)	Coulometric technique w/o diaphragm (HYDRANAL Coulomat AK)
Acetaldehyde	x		
2-Anisaldehyde	x	x	
Benzaldehyde	x	x	
1,2-Cyclohexane-dione	x	x	x
Acetone	x	x	x
Acetophenone	x	x	x

Table 2 Product listing HYDRANAL K-reagents

Part No.	Brand	Description	Package Size
34816	Fluka	HYDRANAL Composite 5 K	500 mL, 1 L, 2 L
34738	Fluka	HYDRANAL KetoSolver	500 mL, 1 L
34698	Fluka	HYDRANAL Medium K	1 L
34817	Fluka	HYDRANAL Working Medium K	1 L
34820	Fluka	HYDRANAL Coulomat AK	500 mL
34821	Fluka	HYDRANAL Coulomat CG-K	50 mL

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For details and complete applications on HYDRANAL K-reagents and our other high-quality HYDRANAL reagents for pyridine-free water determination by Karl Fischer titration, please visit our website sigma-aldrich.com/hydranal or contact our HYDRANAL laboratories:

Europe and Rest of World

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 North America
545 S. Ewing Ave.
St. Louis MO 63103
Help Line: +1-800-493-7262
(toll-free hotline for USA and Canada)
Fax: +1-314-286-6699
E-mail: doug.clark@sial.com

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