



Water determination in aldehydes and ketones

HYDRANAL™ Laboratory Report L 676

(Extract from HYDRANAL Manual, chapter 9.6)

Both aldehydes and ketones pose problems with Karl Fischer titration because they form acetals and ketals respectively with conventional KF reagents (Figure 9.6.a). The reaction forms water, which is also titrated, resulting in vanishing end points

and erroneously high water content. With aldehydes a second side reaction, the bisulfite addition, can also occur (Figure 9.6.b). This reaction consumes water and leads to an erroneously low water content.

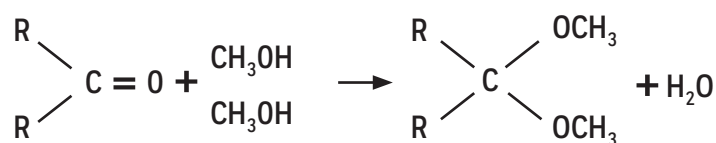


Figure 9.6.a. The formation of acetals or ketals.

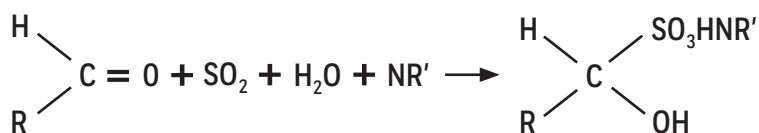


Figure 9.6.b. The bisulfite addition.

NR' = base

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We have investigated the behavior of certain aldehydes and ketones toward the KF titration. The reactivity of aliphatic ketones decreases with increasing chain length. Aromatic ketones are less reactive than aliphatic ketones. Aldehydes are much more reactive than ketones and their tendency to undergo the bisulfite addition is particularly strong.

The formation of acetals and ketals can be suppressed by replacing methanol in the titrating agent with another solvent, typically pyridine or 2-methoxyethanol (methylglycol). However, we found both of these solvents to be unsatisfactory. Pure pyridine alters the

stoichiometry of the KF reaction, enhances the bisulfite addition, and leads to a falsely low water content. 2-methoxyethanol does not sufficiently inhibit the formation of both ketals and acetals and results in a slow titration rate. The levels of water are too high and, because only small samples can be analyzed, the accuracy of the titration is negatively affected.

Our research identified suitable solvents that permit determination of water in aldehydes and ketones without adverse side reactions. These solvents are the basis of the Hydranal™ K-type reagents.

9.6.1 Volumetric titration

As a result of the challenges with KF titration of aldehydes and ketones, we developed special reagents for their determination by volumetric titration:

- Hydranal-Composite 5 K
- Hydranal-Working Medium K
- Hydranal-Medium K
- Hydranal-KetoSolver

The following abbreviated working procedure provides an introduction to their usage.

Procedure 9.6.1.1 Aldehydes and ketones

20–50 mL Hydranal-Working Medium K or Hydranal-Medium K or Hydranal-KetoSolver are added to the titration vessel and titrated to a stable end point with Hydranal-Composite 5 K. The sample is then added and immediately titrated to a stable end point.

By using these reagents and following the recommended titration procedures, the side reactions of acetal or ketal formation and the bisulfite addition are significantly suppressed. Consequently, interferences are not encountered in the titration of aldehydes and ketones. Other techniques can also reduce the influence of these negative side reactions in certain cases, as described in the following discussion.

The bisulfite addition reaction begins upon addition of the sample to the sulfur-dioxide-containing working medium. Therefore, the

KF titration should be started immediately to prevent any water present in the titration vessel from undergoing the bisulfite addition. We utilize the ‘flying start’ method whereby the sample is added within 20 seconds of the start of the titration. The instrument initiates the titration as soon as the sample is added. Titrators should be programmed to add the reagent rapidly for the same reason. However, commercially available instruments vary greatly in this respect.

Despite such precautions, some of the water can still be bound as bisulfite adduct, especially when titrating aromatic aldehydes. The dissociation of the bisulfite adduct must first occur in order to run a reliable determination of the water content in the sample. This is possible by using Hydranal-K reagents since they sufficiently suppress the formation of acetals and ketals.

The amount of water to be titrated should be low enough so that titrations are not inordinately long. We found sample sizes that contain a total of 10–25 mg H₂O are ideal. This amount of water consumes 2–5 mL reagent.

We have investigated the moisture determination of a number of aldehydes and ketones during the development of the Hydranal-K reagents. These compounds are listed in Table 9.6. The table shows the name of the chemical and the water content. The water content given is for reference only and is not to be taken as a limit. Column 3 lists the size of the sample that can be titrated in a 25 mL volume of Hydranal-Working Medium K or Hydranal-Medium K. The entry '10 mL' or '10 g' represents the largest sample size analyzed. Smaller sample sizes are indicated in column 4 with a designation for the reason of the limited sample size:

B = bisulfite addition
I = indication interferences
L = limited solubility
A = buffering of acid

The data in Table 9.6 shows that the determination of water in most ketones is straightforward. 10 mL samples of aliphatic ketones can be titrated without any interference, even with acetone and cyclohexanone, which are particularly reactive.

Procedure 9.6.1.2 Keto-carboxylic acids

25 mL Hydranal-Medium K or Hydranal-Working Medium K or Hydranal-KetoSolver or Hydranal-CompoSolver E are added to the titration vessel, mixed with 0.1–0.5 g Hydranal-Imidazole and titrated to dryness with Hydranal-Composite 5 K. The keto-carboxylic acid sample is then added and titrated in the usual manner.

Keto-carboxylic acids can be titrated according to procedure 9.6.1.2. Exceptions are 2-oxo-propionic acid and 2-oxobutyric acid (alpha-keto acids), which exhibit a strong tendency to undergo the bisulfite addition. The amounts of Hydranal-Imidazole

However, trifluoroacetone gives a noticeable bisulfite addition reaction, so a 'flying start' titration and a verification of end point are required for its reliable determination.

Aromatic ketones and long-chain aliphatic ketones are less reactive and can also be titrated with Hydranal-Composite 5 and Hydranal-Medium K or Hydranal-Working Medium K or Hydranal-KetoSolver or Hydranal-CompoSolver E (the use of Hydranal-Composite 5 K is not necessary). Most heterocyclic ketones perform similarly to aromatic ketones. With acetyl pyridine the bisulfite addition is apparently activated by the pyridyl group, and therefore interferes with the water determination.

Diketones usually behave like normal ketones. Exceptions are diacetyl ketone and 1,2-cyclohexanedione to a certain extent. The adjacent keto groups, particularly in diacetyl ketone, are very reactive and only small amounts of sample can be analyzed. This is not the case with benzyl ketone presumably due to the aromatic substituents present in this compound.

Keto-carboxylic acids shift the pH of the working medium and delay the course of the titration. Buffering the working medium slightly accelerates the titration and restores the pH.

added must be kept small since this reagent enhances the bisulfite addition.

The pH of the working medium is not shifted by the esters of keto-carboxylic acids, and they can be titrated according to procedure 9.6.1.1.

Many aldehydes can be analyzed in a similar manner. The formation of acetals cannot be detected under these titration conditions. On the other hand, the bisulfite addition takes place very rapidly and the sample sizes usually have to be reduced. The 'flying start' method is a good way of reducing the influence of the bisulfite addition.

Aromatic aldehydes are less reactive and consequently present fewer problems. Aliphatic aldehydes are more reactive. The formation of acetal with acetaldehyde is particularly strong, and a sample size of only 2 mL should be used for the titration. The reactivity decreases with increasing chain length and the sample size can be increased to 5 mL starting with butyraldehyde (see L 248).

Formaldehyde does not undergo acetal formation and can be titrated with methanolic reagents as in standard volumetric procedures.

However, the total water content cannot be determined. Typically only 50% H₂O is found in a 35% formaldehyde solution. Part of the water is bound as paraformaldehyde. The total water content can be determined by carrying out the titration at 50°C. Details can be found in Laboratory Reports L 006 and L 386.

A glyoxal solution (40%) behaves similarly to formamide and can be titrated at elevated temperature (L 267). With a glutaraldehyde solution (50%) we titrated free water at room temperature and total water content at 50°C.

Table 9.6. Titration procedures for aldehydes and ketones.

SUBSTANCE	WATER CONTENT	TOTAL AMOUNT	RESTRICTION
Aliphatic ketones			
Acetone	0.064%	10 mL	
Methyl-n-propyl ketone	0.22%	10 mL	
Methyl-isobutyl ketone	0.041%	10 mL	
Ethyl-isobutyl ketone	0.39%	10 mL	
Allyl acetone	0.19%	10 mL	
3-Octanone	0.082%	10 mL	
2-Decanone	0.080%	10 mL	
Dihexyl-ketone	0.0086%	5 g	I
Cyclohexanone	0.032%	10 mL	
1,1,1-Trifluoroacetone	0.25%	10 mL	B
Hexachloroacetone	0.12%	5 mL	I
Aromatic ketones			
Acetophenone	0.029%	10 mL	
2-Fluoroacetophenone	0.21%	10 mL	
2,4-Dihydroxyacetophenone	0.021%	5 g	L
2-Aminoacetophenone	0.13%	10 mL	
Benzylmethyl ketone	0.038%	10 mL	
Benzylacetone	0.64%	10 mL	
Benzophenone	0.0032%	5 g	I
Benzoin	0.043%	2 g	L
Heterocyclic ketones			
2-Acetylpyridine	0.39%	10 mL	B
2-Pyrrolidone	0.058%	10 mL	
N-Methyl-2-pyrrolidone	0.021%	10 mL	
2-Benzoylpyridine	0.016%	10 g	
3-Acetylundol	0.34%	2 g	L
Diketones			
Diacetyl	0.10%	1 mL	B
Acetylacetone	0.043%	10 mL	
2,5-Hexandione	0.32%	10 mL	
1,2-Cyclohexanedione	0.90%	1 g	B
Benzoylacetone	0.037%	10 g	
Benzil (Dibenzoyl)	0.032%	10 g	
Dibenzoylmethane	0.036%	10 g	
Keto-carboxylic acids and derivatives			
2-Oxo-propionic acid	1.07%	10 mL	B, A
2-Oxo-butyric acid	0.95%	1 g	B, A
Levulinic acid	0.22%	10 mL	A
3-Phenyl propionic acid	0.020%	5 g	L
2-Acetylbenzoic acid	0.079%	5 g	L, A
2-Benzoyl benzoic acid	0.94%	10 mL	
Ethyl acetoacetate	0.52%	10 mL	
Ethyl levulinate	0.057%	10 mL	
Ethyl benzoylacetate	0.033%	10 g	
Aliphatic aldehydes			
Acetaldehyde	0.021%	2 mL	B
Propionaldehyde	0.15%	2 mL	B
n-Butyraldehyde	0.035%	5 mL	B
Crotonaldehyde	0.10%	5 mL	B
Octaldehyde	0.26%	5 mL	B
Glycolaldehyde	0.25%	1 g	B, L
Chloral	0.12%	10 mL	exothermic
Chloral hydrate	10.86%	0.5 g	high water content
Bromal		0	I
Paraldehyde	0.018%	10 mL	
Cyclohexane carbaldehyde	0.027%	5 mL	
Diphenylacetaldehyde	0.11%	10 mL	B
Acetaldehyde diethylacetal	0.029%	10 mL	
Bromoacetaldehyde diethylacetal	0.043%	10 mL	I
Aromatic aldehydes			
Benzaldehyde	0.13%	5 mL	B
2-Bromobenzaldehyde	0.10%	2 mL	B
Salicylaldehyde	0.027%	10 mL	
3-Hydroxybenzaldehyde	0.22%	5 g	B
2-Anisaldehyde	0.040%	10 mL	B
4-Dimethylaminobenzaldehyde	0.016%	10 g	
Phenylglyoxal	1.00%	0.5 g	B

B = bisulfite addition, I = indication interferences, L = limited solubility, A = buffering of acid

9.6.2 Coulometric titration

We have also developed reagents for the coulometric determination of water in ketones:

- Hydranal-Coulomat AK
- Hydranal-Coulomat CG-K

Hydranal-Coulomat AK is the anolyte and is added to the anodic compartment of the titration cell. Hydranal-Coulomat CG K is the corresponding catholyte.

The solvent system of each reagent has been carefully made up to meet the demands of ketone analysis using modern KF instruments. The composition of these reagents has been optimized and should not be altered by the addition of other solvents. For the same reason, no more than 20 mL of liquid sample per 100 mL of the anolyte reagent should be used. The same restrictions apply to the analysis of solids dissolved in solvents. We recommend a 4:1 (v/v) solution of 2-methoxyethanol and Hydranal-Chloroform, or the solvents used individually, because they ensure minimal alteration to the electrolytic properties of the anolyte.

Use of methanol as the solvent is particularly detrimental because it enhances the formation of ketals. The coulometric titration cell must be thoroughly cleaned when replacing conventional methanol-containing coulometric reagents with Hydranal K-type reagents. If ketones are analyzed on a regular basis, we recommend having a separate coulometric titration cell dedicated to this analysis to prevent the need for frequent cleaning or the possibility of methanol contamination.

Iodine solutions based on methanol must not be used to dry the reagents used in the ketone titration cell. We recommend the use of Hydranal-Composite 5 or a solution of iodine in diethylene glycol monoethyl ether.

The K-type reagents can be used in the usual way for the determination of water in ketones. The samples sizes should be relatively small, preferably 1 mL. The sample size of reactive ketones, such as cyclohexanone, should only be 0.2 mL or 0.5 mL. Larger samples can cause serious instrument drift and eventually an end point will not be reached. The instrument also influences the sample size.

After several ketone samples have been analyzed in the K-type reagent, the instrument indicates a drift or a residual current. This drift corresponds to the amount of water that the instrument removes per minute. This also means that in a drifting cell there is a continual consumption of reagent. It is therefore understandable that a titration cell that has been used for a number of successive ketone titrations will have a permanent consumption of reagent. The reagent in the cell will be spent within a few days even if it has not been used for the titration of further samples.

Aldehydes can be analyzed with the same reagents but with some restrictions. Aldehydes undergo the same side reactions, but more rapidly than corresponding ketones. The water content of benzaldehyde, representative of aromatic aldehydes, can be determined with an acceptable degree of accuracy if the sample size is restricted to 0.5 mL. Aromatic aldehydes undergo the bisulfite addition and, like ketones, the dissociation of the bisulfite adduct must occur first in order to run a reliable determination of the water content in the sample. The acetal formation with n-butyraldehyde is particularly strong and the delay time of the instrument should not be set too high. This side reaction decreases with increasing chain length. Side reactions predominate in acetaldehyde to such an extent that it cannot be analyzed.



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An accurate determination of water in aldehydes should be carried out using the volumetric titration with Hydranal-Composite 5 K and Hydranal-Medium K or Hydranal-Working Medium K or Hydranal-KetoSolver. Hydranal-Coulomat AK and Hydranal-Coulomat CG-K can also be used to investigate other compounds, such as hydrocarbons, halogenated hydrocarbons, or alcohols. They are not suitable for the analysis of acids and bases.

Using the same reagent for the determination of the water content of a mixture of ketones and other substances is possible if the

substance does not chemically react with the ketone. Therefore, alcohols cannot be investigated in the presence of ketones.

We have found it economical and practical to titrate aldehydes/ketones and other compounds in separate, dedicated cells. The standard reagents for coulometry, Hydranal-Coulomat A/AG/AG-H/E and Hydranal-Coulomat CG, have a significantly higher water capacity than the Hydranal-K reagents.



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