Solstice

ACCURATE WATER DETERMINATION IN KETONES WITH HYDRANAL™ NEXTGEN COULOMAT A-FA AND C-FA

The First Commercially Available Karl Fischer Titration Reagents
Free of Alcohol and Free of Imidazole

INTRODUCTION

In organic chemistry, carbonyl compounds are a functional group of compounds that contain a carbon atom with a double bond to an oxygen atom. Many different kinds of carbonyl compounds are present in nature, some of them being illustrated in Fig. 1.

While the Karl Fischer (KF) titration of amides, esters, and most carboxylic acids can be performed without any issues, the titration of aldehydes and ketones can be challenging. For example, in the presence of alcohols, the later form acetals (Fig. 2-1) and ketals (Fig. 2-2), which is accompanied by the formation of water, resulting in vanishing or no endpoints, and erroneously large water amounts. Furthermore, aldehydes undergo an additional side reaction [the bisulfite addition reaction (Fig. 2-3)], which consumes water and leads to erroneously low water content. Finally, the Iodoform reaction (Fig. 2-4) can disturb the KF analysis of ketones, whereby iodine is consumed, resulting in unstable titration endpoints and incorrect, large water results.

In the Hydranal laboratory report L676, we show that 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, due to their smaller steric hindrance, and their tendency to undergo the bisulfite addition.

The formation of acetals and ketals can be reduced by replacing methanol in the titrating reagent with other solvents, such as chloroform and sterically hindered alcohols. The bisulfite reaction can be reduced by decreasing the amount of SO_2, and the iodoform reaction can be delayed, for example, by lowering the amount of base in the KF reagent.

Since most of the shown side reactions exist as an equilibrium, it is not possible to stop all of the undesirable side reactions completely. However, by choosing the right reagent composition, side reactions can be suppressed as best as possible and reaching the KF titration endpoint is feasible.

With increasing sample load, the reagent becomes more and more inaccurate. That is especially true for the coulometric KF methodology, and therefore, there is always a compromise between “accepting errors”, or not being able to titrate a ketone sample by coulometric KF titration at all.

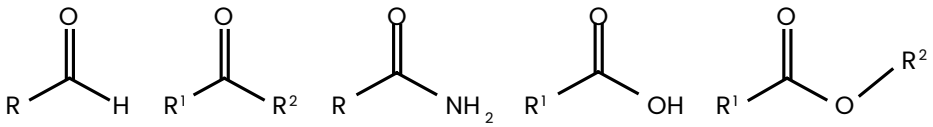


Fig. 1. Common carbonyl compounds

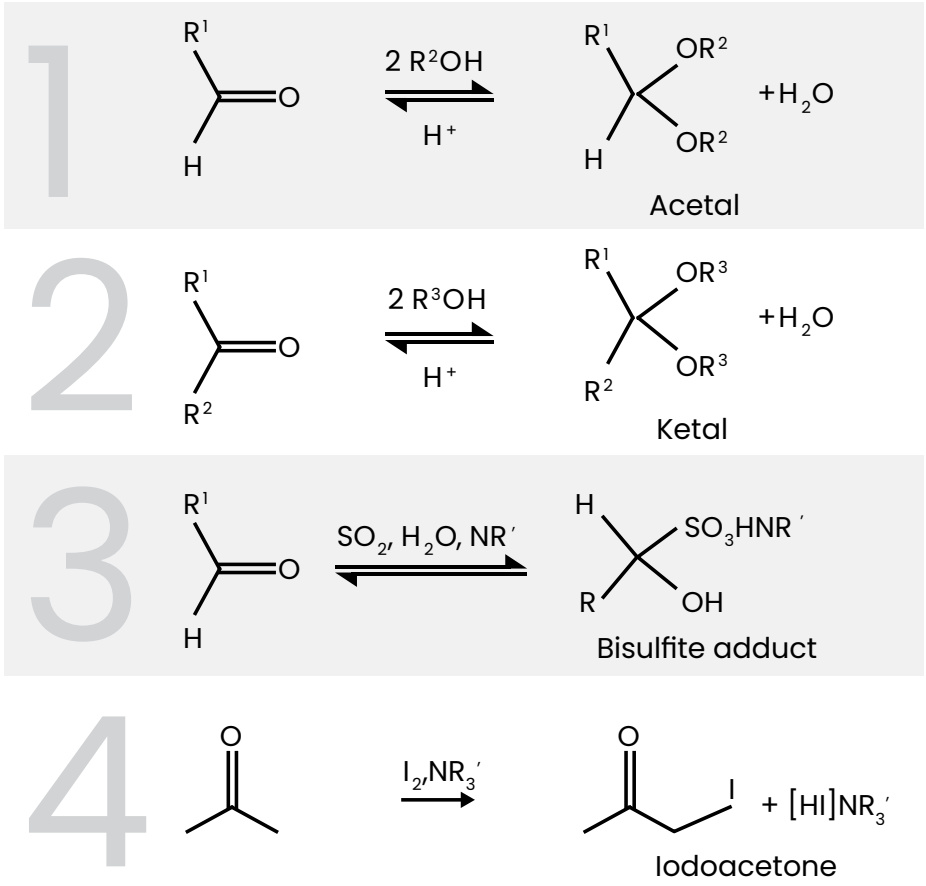


Fig. 2. Different types of side reactions in KF titration medium

COULOMETRIC WATER DETERMINATION IN KETONE SAMPLES USING THE NOVEL HYDRANAL FA REAGENTS

Until now, Hydranal offered the Coulomat-AK reagent as anolyte and the Coulomat CG-K reagent as catholyte for the coulometric titration of ketones. AK/CG-K are methanol-free reagents that make it possible to analyze approximately 20 mL of ketone samples (e.g. 40 x 0.5 mL). The accuracy decreases with increasing start drift values. Generally, the highest accuracy is obtained when the start drift is below 20 µg/min. After the introduction of a certain amount of ketone sample into the titration cell, an auto drift increase starts, which unfortunately destroys the cell performance after one or two days. To overcome this, Solstice has developed the Hydranal NEXTGEN Coulomat A-FA and Coulomat C-FA products, which are the world's first alcohol-free KF titration reagents. These FA reagents – which stands for "free of alcohol" – have the advantage that alcohol-related side reactions, such as ketal formation do not occur. That is why Coulomat A-FA/C-FA enables the analysis of more ketone samples with lower start drift values and higher accuracy. Furthermore, one vessel filling FA reagents can be used over a longer period.

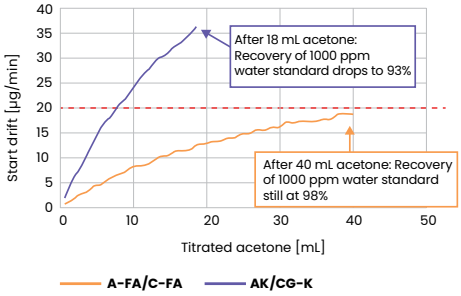


Fig. 3. *Titration of "pure" acetone (1 mL portion) in Hydranal NEXTGEN Coulomat A-FA/C-FA and Coulomat AK/CG-K, respectively.*

Figure 3 illustrates the superior performance of the new Hydranal NEXTGEN Coulomat FA reagents in the titration of "pure" acetone, in comparison to that of Hydranal Coulomat AK/CG-K reagents. When using Coulomat AK/CG-K, the start drift increases above 20 µg/min after the titration of approx. 8 mL of "pure" acetone. However, when Hydranal NEXTGEN Coulomat FA reagents are used, the start drift keeps below 20 µg/min even after the titration of 40 mL of "pure" acetone. Also, the recovery of 1000 ppm water stays at 98%, whereas the recovery of Coulomat AK/CG-K already drops to 93% after the titration of 18 mL of "pure" acetone.

Through this experiment, we were also able to show that "pure" acetone exhibits a different titration behavior than "impure" acetone.[1] In the case of "impure" acetone samples, the drift value increases much more than in that of "pure" acetone samples. Also, the recovery values decrease significantly faster in the case of "impure" acetone samples.

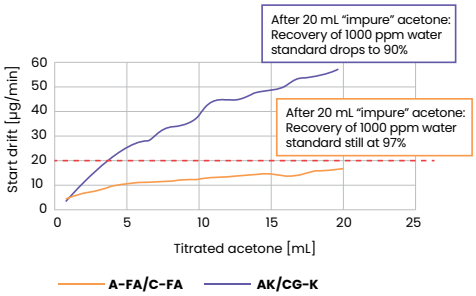


Fig. 4 *Titration of "impure" acetone (1 mL portion) in Hydranal NEXTGEN Coulomat A-FA/C-FA and Coulomat AK/CG-K, respectively.*

Figure 4 illustrates the fact that, when using Hydranal Coulomat AK/CG-K, the start drift increases above 20 µg/min after the titration of approx. 3 mL of "impure" acetone, while when Hydranal NEXTGEN Coulomat FA reagents are used, the start drift stays below 20 µg/min, even after the titration of 20 mL of "impure" acetone.

1. "Pure" acetone is free of decomposition products, while "impure"acetone is mostly contaminated with methyl ethyl ketone, methyl isobutyl ketone, and higher acetone condensation products (self-decomposition of acetone).

EXAMPLE TITRATION RESULTS

One of the main advantages of the new Hydranal NEXTGEN Coulomat A-FA and C-FA reagents is the potential to successfully measure many different ketone samples in one vessel filling. To check the accuracy of obtained results, water standard samples were tested for water recovery before each series of the same samples. Additionally, the drift value was monitored before each titration. The results of such measurement series are shown in Tables 1 and 2. In all cases, the obtained water results provided high accuracy, and water recovery for the 1002 ppm water standard was in the range of 97-99%.[2]

NO.	SAMPLE TYPE	SAMPLE SIZE [mL]	WATER RESULT [ppm]	WATER RESULT [µg]	TITRATION TIME [s]	START DRIFT [µg/min]	WATER RECOVERY [%]
1	**Water Standard 1002 ppm**	1	993.2	978.3	103	2.2	**99**
2	**Methyl levulinate**	1	72.0	70.9	60	1.4	
3	**Methyl levulinate**	1	72.5	76.1	58	1.7	
4	**Methyl levulinate**	1	72.3	75.1	60	2.1	
5	**Methyl levulinate**	1	72.4	75.7	62	2.1	
6	**Methyl levulinate**	1	71.6	75.3	60	2.6	
7	**Methyl levulinate**	1	72.2	75.9	61	2.1	
8	**Methyl levulinate**	1	71.5	73.4	62	2.7	
9	**Methyl levulinate**	1	70.9	76.6	60	3.3	
10	**Methyl levulinate**	1	71.4	70.6	61	3.0	
11	**Methyl levulinate**	1	70.9	68.7	62	3.4	
12	**Water Standard 1002 ppm**	1	989.8	1003.8	120	2.9	**99**
13	**Methyl acetoacetate**	1	27.2	30.0	48	2.7	
14	**Methyl acetoacetate**	1	27.6	29.9	54	3.4	
15	**Methyl acetoacetate**	1	26.8	29.7	49	4.5	
16	**Methyl acetoacetate**	1	27.7	29.7	45	3.9	
17	**Methyl acetoacetate**	1	27.2	29.6	45	4.5	
18	**Methyl acetoacetate**	1	27.0	28.6	47	5.1	
19	**Methyl acetoacetate**	1	27.6	29.6	46	4.5	
20	**Methyl acetoacetate**	1	27.4	29.7	47	4.7	
21	**Methyl acetoacetate**	1	28.6	29.4	44	4.8	
22	**Methyl acetoacetate**	1	28.0	28.1	45	5.3	
23	**Water Standard 1002 ppm**	1	979.7	992.1	110	5.8	**98**
24	**2-Butanone**	1	4.4	3.7	40	5.2	
25	**2-Butanone**	1	3.6	2.9	34	5.8	
26	**2-Butanone**	1	5.5	4.4	37	5.8	
27	**2-Butanone**	1	3.6	3.5	39	6.1	
28	**2-Butanone**	1	3.3	2.1	32	7.2	
29	**2-Butanone**	1	3.6	2.7	33	7.4	
30	**2-Butanone**	1	2.5	2.1	34	8.1	
31	**2-Butanone**	1	3.2	2.6	33	8.2	
32	**2-Butanone**	1	3.0	2.3	33	8.8	
33	**2-Butanone**	1	3.3	2.5	28	8.6	
34	**Water Standard 1002 ppm**	1	975.7	965.1	128	8.9	**97**

Table 1. *Successive titrations of* ***reactive ketone*** *samples in one vessel filling using 100 mL Hydranal NEXTGEN Coulomat A-FA in the anodic chamber and 5 mL Hydranal NEXTGEN Coulomat C-FA in the cathodic chamber.*

2. For best results, the water recovery of a 1000 ppm water standard should be in the range of 97-103%.

NO.	SAMPLE TYPE	SAMPLE SIZE [mL]	WATER RESULT [ppm]	WATER RESULT [µg]	TITRATION TIME [s]	START DRIFT [µg/min]	WATER RECOVERY [%]
1	**Water Standard 1002 ppm**	1	995.3	938.4	97	1.9	**99**
2	**4-Methyl-2-pentanone**	1	197.3	157.0	93	2.8	
3	**4-Methyl-2-pentanone**	1	200.5	160.0	92	1.4	
4	**4-Methyl-2-pentanone**	1	188.8	150.6	92	2.0	
5	**4-Methyl-2-pentanone**	1	189.1	150.6	93	1.9	
6	**4-Methyl-2-pentanone**	1	189.2	144.2	92	2.1	
7	**4-Methyl-2-pentanone**	1	188.8	153.0	95	1.8	
8	**4-Methyl-2-pentanone**	1	188.7	151.1	97	2.0	
9	**Water Standard 1002 ppm**	1	992.6	1054.6	103	3.9	**99**
10	**Acetylacetone**	1	563.8	568.1	85	4.2	
11	**Acetylacetone**	1	562.0	541.9	82	6.5	
12	**Acetylacetone**	1	561.7	552.7	79	8.6	
13	**Acetylacetone**	1	561.0	552.2	75	10.2	
14	**Acetylacetone**	1	561.2	521.3	75	11.8	
15	**Water Standard 1002 ppm**	1	991.5	996.3	89	13.3	**99**
16	**Cyclohexanone**	0.5	93.9	46.7	61	12.6	
17	**Cyclohexanone**	0.5	93.3	44.8	59	15.4	
18	**Cyclohexanone**	1	92.3	88.1	73	17.2	
19	**Cyclohexanone**	0.5	95.0	44.5	58	22.4	
20	**Cyclohexanone**	0.5	94.6	44.7	61	24.6	
21	**Water Standard 1002 ppm**	1	980.5	1000.5	94	26.9	**98**

Table 2. *Successive titrations of* ***reactive ketone*** *samples in one vessel filling using 100 mL Hydranal NEXTGEN Coulomat A-FA in the anodic chamber and 5 mL Hydranal NEXTGEN Coulomat C-FA in the cathodic chamber.*

TEST METHODOLOGY

REAGENTS

Tests were performed using 100 mL 34471 Hydranal NEXTGEN Coulomat A-FA as anolyte and 5 mL 34470 Hydranal NEXTGEN Coulomat C-FA as catholyte.

At the beginning, in between, and after each series of titrations, 1 mL of 34828 Hydranal-Water Standard 1.0 was titrated to confirm the recovery and reliability of results.

The titration tests were performed with sample sizes in a range of 0.5-1 mL. All calculations were based on differential weighing on analytical balance.

TITRATION DEVICE

Titration device was performed on Metrohm 852 Titrando titrator with a generator electrode with diaphragm. Prior to the test, all titration cell parts including generator electrode, stirring bar and glass stopper, were dried in the oven at 50°C for two hours. The fresh titration vessel was pre-conditioned for one hour to a stable and low drift below 10 µg/min. Afterwards, the drift was stabilized between each titration for 70-100 s. Drift correction was turned on. Minimum titration time was 25 s.

The titration parameters used for these tests are shown in Table 3.

TITRATION PARAMETERS	
Polarization current	10 µA
Gen. current	auto
End point	50 mV
Dynamics	70 mV
Max. rate	max. µg/min
Min. rate	15 µg/min
Extraction time (min. titration time)	25 s
Rel. stop drift	5 µg/min
Stirring speed	8
Start drift	30 µg/min
Drift correction	auto
Stop time	off
Stability time	70 s
Pause	0 s

Table 3. *Titration parameters*

CONCLUSION

> The new Hydranal NEXTGEN Coulomat A-FA and C-FA reagents enable the accurate measurement of water content in many different types of ketone samples with high accuracy and lower starting drifts.

Until now, in standard alcoholic KF reagents, ketone samples caused significant side effects, leading to an increase in drift and lower accuracy of measurement.

The new alcohol-free formulation of Hydranal NEXTGEN Coulomat A-FA and C-FA reagents avoids alcohol-related side effects and allows for accurate water determination, even in difficult samples. Additionally, the new formulation does not contain CMR (carcinogenic, mutagenic and reprotoxic) substances or halogenated hydrocarbons, making them safer for users.



THE HYDRANAL ADVANTAGE: DEDICATED TECHNICAL SUPPORT

With 40 years of experience, Hydranal offers unparalleled global technical support in the field of Karl Fischer titration. Our team of experts is happy to address your questions and can be contacted directly via email at hydranal@solstice.com or at any of our live seminars and webinars.



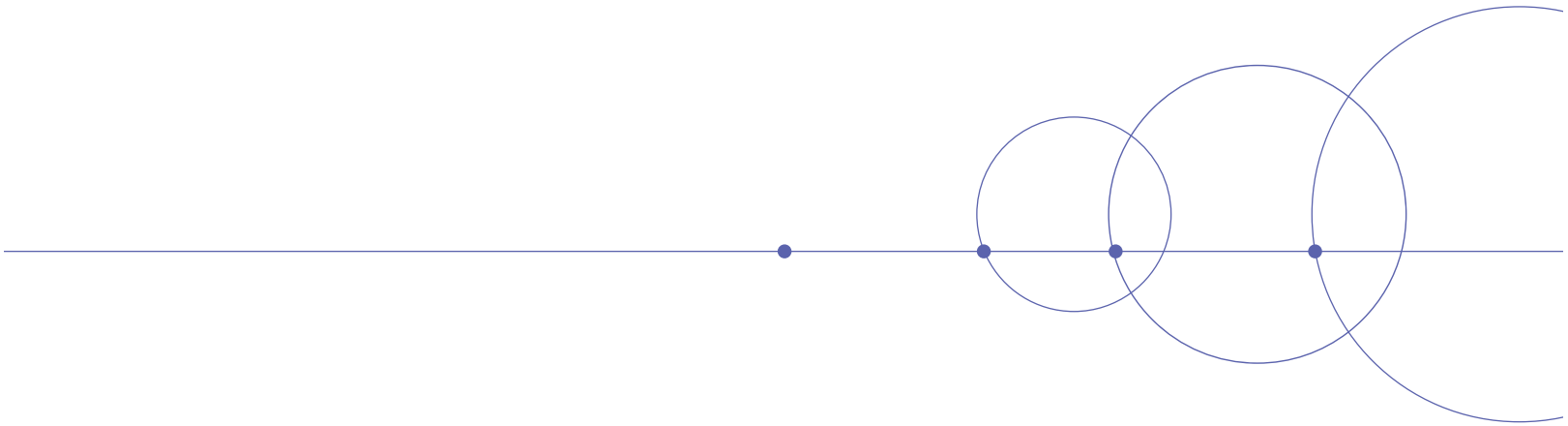
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1603104-ESM-WPR-Hydranal-Ketones-FA | SOLS | 06/26