



WHITE PAPER

Water content determination in ketones using Hydranal™ NEXTGEN FA reagents

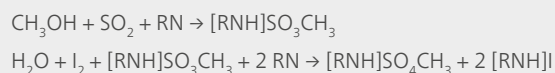
Ketones react with the alcohol component in Karl Fischer (KF) reagents. The ketal formation releases water, thereby increasing the water content and falsifying the titration results. This side reaction depends on the reactivity of the respective ketone, and its influence is even more pronounced in **coulometric KF titration**.

Previous generation coulometric KF reagents only suppress this side reaction to an extent. Even though they do not contain methanol, they always contain an alcohol component. The presence of alcohol in KF reagents results in a stoichiometric reaction of 1:1 between water and iodine. Without alcohol, the stoichiometry is changed, resulting in a 2:1 reaction of water with iodine (i.e., the Bunsen reaction).

The Hydranal™ NEXTGEN FA reagents from Honeywell do not contain any alcohol; here, FA is an abbreviation for «free of alcohol». The Bunsen reaction is suppressed with methanesulfonic acid which is present as a stabilizer in these reagents, therefore resulting in a 1:1 reaction of water and iodine. With Hydranal™ NEXTGEN FA reagents, the water content in ketones can be determined quickly and reliably. Compared to other existing KF reagents for ketones on the market, the side reactions are measurably better suppressed when using Honeywell Hydranal™ NEXTGEN FA reagents.

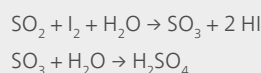
INTRODUCTION

When using alcohol-based Karl Fischer reagents, the following two reactions occur as postulated by Dr. Eugen Scholz [1]:



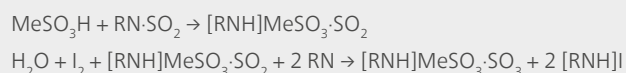
First, an alkyl sulfurous acid is formed. When in the presence of water and iodine, the alkyl sulfurous acid is oxidized to form alkyl sulfuric acid. In this case, water and iodine react in a molar ratio of 1:1.

Without an alcohol group, there is no formation of an alkyl sulfurous acid. As a result, the stoichiometry of the reaction in unmodified alcohol-free KF reagents is different, and the molar ratio of water and iodine is 2:1 (Bunsen reaction):



Coulometric Hydranal FA reagents from Honeywell are based on an acetonitrile solvent. Additionally, 1-ethylimidazole replaces imidazole, a known CMR (carcinogenic, mutagenic, and reprotoxic) substance, and methanesulfonic acid (MSA) is added to stabilize the reagent.

Hydranal experts postulate that similar to alcohols, the MSA forms a complex with sulfur dioxide and suppresses the Bunsen reaction. Therefore, the molar ratio of water and iodine is 1:1 once more, as shown in the following reaction mechanisms.



Alcohol-based Karl Fischer reagents can have different colors depending on their conditioning state. However, this does not apply to alcohol-free KF

reagents. The color of the solution is very similar, no matter whether the titration cell is conditioned or if it still contains water (**Figure 1**). Considering that it is recommended to use a titration cell made of amber-colored glass, this is not a disadvantage.

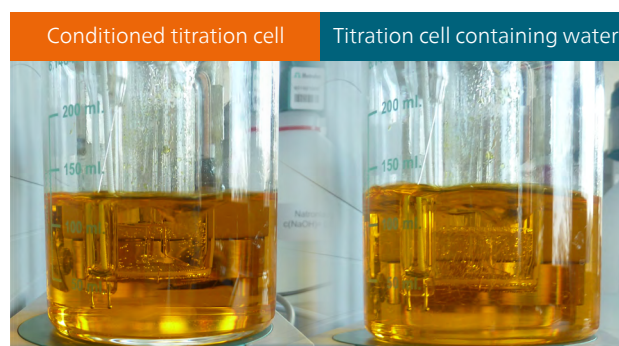


Figure 1. Comparison of a conditioned (L) and an unconditioned (R) titration cell when using Karl Fischer reagents that do not contain alcohol.

According to Honeywell, the Hydranal™ NEXTGEN FA reagents tend to release iodine depending on the storage conditions. This excess iodine must be removed by adding water in acetonitrile before the conditioning step can begin.

PHOTOSENSITIVITY

Hydranal™ NEXTGEN FA reagents are photosensitive, which can lead to very low drift values.

Direct exposure to light (e.g., sunlight, fluorescent tubes, daylight lamps) results in an excess of iodine in the titration cell within a few (10–20) minutes, even if the generator electrode does not generate any iodine. The release of this excess iodine can influence the titration.

Placing the titration cell in a shady corner of the laboratory is sufficient. To completely avoid the light-induced release of iodine, the use of an aluminum foil-covered titration cell, a printable Hydranal™ UV-SHIELD, or an amber-colored glass titration cell is strongly recommended (**Figure 2**).



Figure 2. Clear glass titration cell covered with aluminum foil (L) and amber glass titration cell (R).

To investigate the photosensitivity and the effectiveness of the amber-colored glass titration cell to prevent the light-induced side reaction, both titration cells (clear and amber) were exposed to an LED spotlight. Both the intensity and color temperature of the spotlight were infinitely variable. The experimental setup is shown in **Figure 3**.

Initially, the baseline drift in the aluminum-covered clear glass titration cell was determined. After two minutes, the aluminum cover was removed to fully expose the clear glass titration cell to the LED spotlight. The measured potential was recorded and

considered a qualitative measure for the excess of iodine.

No influence on the measured potential was observed for the clear glass titration cell when it was covered with aluminum foil. After removing the aluminum cover from the clear glass titration cell, a strong side reaction causing the release of iodine could be observed when the cell was illuminated with 2200 lumens and 3200 K or 5600 K, respectively (light green and dark grey lines in **Figure 4**).

No influence was observed for the amber glass cell.



Figure 3. Experimental setup to study the photosensitivity of the Hydranal alcohol-free KF reagents.

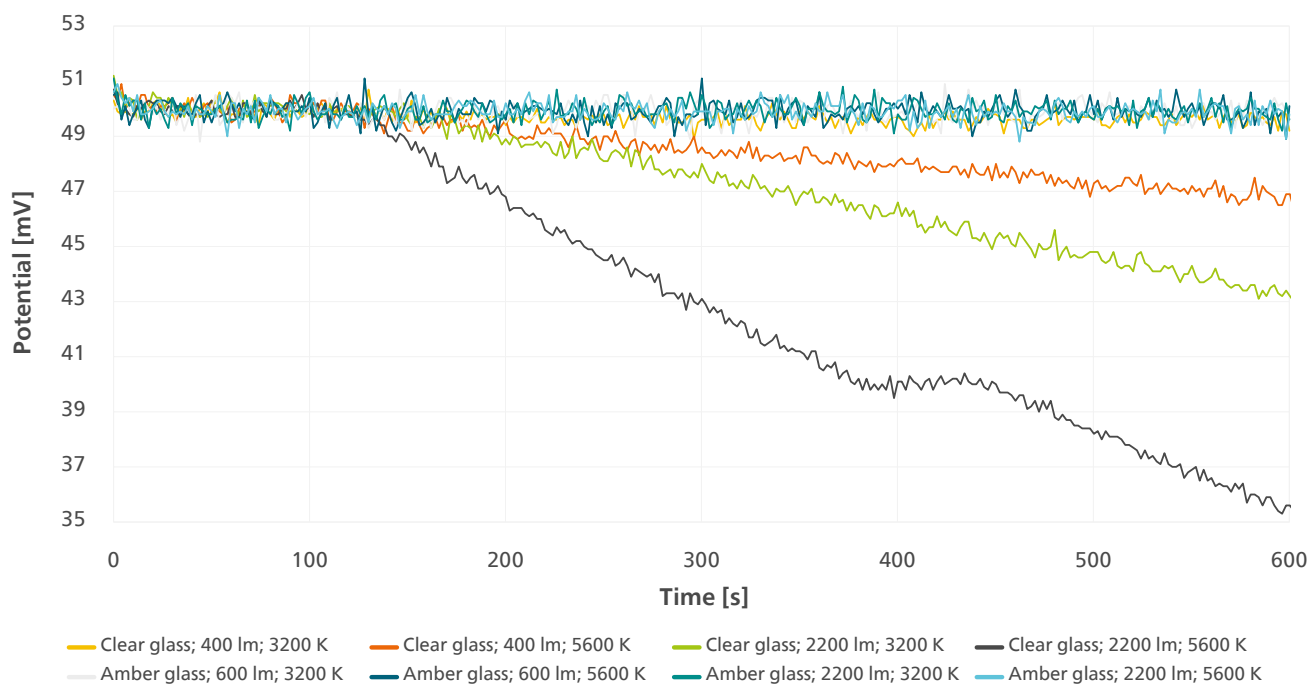


Figure 4. Plot of potential against time; time of illumination: 120 s.

RECOMMENDED PARAMETERS

According to Honeywell, the standard parameters for coulometric Karl Fischer titration using a generator electrode with diaphragm can be used for the FA reagents. However, 30 s was defined as the stabilizing time.

Table 1. Recommended parameters for coulometric Karl Fischer titration with Hydranal™ NEXTGEN FA reagents.

General/Hardware	
Titration mode	KFC
Parameters for conditioning	
Start drift [$\mu\text{g}/\text{min}$]	20
Stabilizing time [s]	30
Sample addition time [s]	8
Correction with amount drift	Automatic
Conditioning stop time	Off
Endpoint control parameters	
Endpoint at [mV]	50
Control range [mV]	70
Maximum generator rate [$\mu\text{g}/\text{min}$]	Maximum
Minimum generator rate [$\mu\text{g}/\text{min}$]	15.0
Stop criterion	Relative stop drift
Relative stop drift [$\mu\text{g}/\text{min}$]	5
Titration parameter	
Extraction time [s]	0
I(pol) [μA]	10
Generator type	With diaphragm
Generator current [mA]	Automatic
Stop conditions	
Stop time [s]	Off

MEASUREMENTS

The experiments were carried out using an 851 Titrando (2.851.0010) equipped with an 801 Stirrer (2.801.0010). As test solutions, two different **water standards** (Hydranal Water Standard 1.0 and Hydranal Water Standard 0.1 PC) plus several ketones (including **acetone**, **butanone**, **1-methyl-2-pyrrolidone**, **2,4-dimethyl-3-pentanone**, and **acetylacetone**) were used.

– WATER STANDARDS

The recovery rates of the determined water standards were close to 100% (**Tables 2 and 3**). The 0.1 mg/g (100 µg/g) water standard showed a slightly higher recovery rate of approximately 102% (**Table 3**). However, this result lies in the range of 90–110% suggested by the EDQM [2].

Table 2. Results for Hydranal Water Standard 1.0.

Sample size [g]	Water content [µg/g]	Recovery [%]
0.8856	1003	100.4
0.8745	994	99.5
1.1866	991	99.2
Mean value	996	99.7
SD abs.	6	0.6
SD rel. in %	0.6	0.6

Table 3. Results for Hydranal Water Standard 0.1 PC.

Sample size [g]	Water content [µg/g]	Recovery [%]
1.7526	106	101.9
1.4518	106	102.1
1.3087	106	101.8
Mean value	106	101.9
SD abs.	0	0.1
SD rel. in %	0	0.1

– ACETONE

Water content determinations in acetone work well with the tested alcohol-free Hydranal KF reagents from Honeywell. The determination time of acetone p.a. is between 1–3 minutes (**Table 4**). For acetone spiked with approximately 2% of water, the determination time increased to between 2–9 minutes (**Table 5**). The endpoints were found reliably using the recommended parameters from **Table 1**.

Table 4. Results for acetone p.a.

Sample size [g]	Water content [µg/g]
2.0258	244
3.3080	245
2.1314	245
1.2285	251
1.0054	245
0.9150	253
0.8911	250
1.1296	250
0.5770	253
Mean value	248
SD abs.	4
SD rel. in %	1.5

Table 5. Results for acetone spiked with approximately 2% water.

Sample size [g]	Water content [µg/g]
0.3541	23224
0.2286	23169
0.3400	23096
0.1478	23222
0.1617	23192
0.1348	22978
0.0569	23102
0.1196	22866
0.0745	22982
Mean value	23092
SD abs.	126
SD rel. in %	0.5

The drift increased slightly after every sample addition. However, the recovery rate of a water standard was roughly the same before (102.0%) and after (102.7%) the water content determination of 18 acetone samples (**Table 6**). The total amount of acetone added was approximately 14.2 g.

Table 6. Comparison of the recovery rate of Hydranal Water Standard 0.1 PC before and after the measurement of 18 acetone samples.

Recovery:	Before acetone addition [%]	After acetone addition [%]
	101.6	102.9
	102.2	102.6
	102.3	102.7
Mean value	102.0	102.7
SD abs.	0.41	0.11
SD rel. in %	0.4	0.1

– BUTANONE

Compared to the measurements with acetone, the determination times were shorter for butanone—less than 70 s for the pure sample (**Table 7**), and between 100–180 s for the sample spiked with approximately 1% of water (**Table 8**). A drift increase after every determination was also observed for butanone. This factor could lead to higher standard deviations if the measurements are carried out without enough conditioning time given between the single measurements.

The recovery rates of Hydranal Water standard 1.0 before and after a measurement series of 15 samples of butanone were 98.4% and 99.8%, respectively (**Table 9**).

Table 7. Results for butanone puriss.

Sample size [g]	Water content [µg/g]
0.3832	843
0.1904	680
0.3715	676
0.2719	650
0.2079	651
0.1444	648
Mean value	691
SD abs.	76
SD rel. in %	10.9

Table 8. Results for butanone spiked with water.

Sample size [g]	Water content [µg/g]
0.0992	10836
0.0933	11207
0.1339	10906
0.0835	10789
0.1375	10915
0.1068	10904
0.1972	10855
0.1103	10798
0.1381	10790
Mean value	10890
SD abs.	129
SD rel. in %	1.2

Table 9. Comparison of the recovery rate of Hydranal Water Standard 1.0 before and after measurement of 15 butanone samples.

Recovery:	Before acetone addition [%]	After acetone addition [%]
	99.4	100.1
	96.9	99.2
	99.0	100.1
Mean value	98.4	99.8
SD abs.	1.3	0.5
SD rel. in %	1.3	0.5

– 1-METHYL-2-PYRROLIDONE

Accurate results were obtained for 1-methyl-2-pyrrolidone (**Table 10**). In most cases, an endpoint was found in less than 100 s.

Table 10. Results for 1-methyl-2-pyrrolidone, puriss.

Sample size [g]	Water content [$\mu\text{g/g}$]
0.1978	2258
0.3352	2243
0.1959	2248
0.5699	2251
0.3950	2241
1.3329	2254
Mean value	2249
SD abs.	6
SD rel. in %	0.3

– 2,4-DIMETHYL-3-PENTANONE

The water content determination in 2,4-dimethyl-3-pentanone took significantly longer, between 4–7 minutes (**Table 11**). Even though the start drift was much more constant compared to 1-methyl-2-pyrrolidone, the obtained results exhibited a higher variation. Based on the shape of the coulometric titration curve, a side reaction or an interaction with 1-methyl-2-pyrrolidone must be assumed.

Table 11. Results for 2.4-dimethyl-3-pentanone, p.a.

Sample size [g]	Water content [$\mu\text{g/g}$]
0.1658	2416
0.1322	2468
0.1881	2524
0.1941	2575
0.1935	2586
0.4213	2623
Mean value	2532
SD abs.	78
SD rel. in %	3.1

– ACETYLACETONE

The water content determinations in acetylacetone resulted in accurate results (**Table 12**).

Table 12. Results for acetylacetone for synthesis.

Sample size [g]	Water content [$\mu\text{g/g}$]
0.3307	1219
0.1901	1216
0.1233	1227
Mean value	1221
SD abs.	6
SD rel. in %	0.5

SUMMARY

The water content determination in ketones is fast and reproducible with the Hydranal™ NEXTGEN FA reagents from Honeywell. As the drift increases after every sample addition, it must be assumed that other non-alcohol-related side reactions still occur. Most likely, the symmetrical aldol condensation of two ketone molecules is responsible for the drift increase. However, this side reaction has a much lower impact on the drift increase than the water-releasing ketal formation reaction with alcohols. Regardless, the water content determination of several grams of ketones works without any issues.

References

- [1] Scholz, E. *Karl-Fischer-Titration: Methoden zur Wasserbestimmung*; Springer-Verlag, 2013.
- [2] Council of Europe. Qualification of Equipment - Annex 5: Qualification of Automatic Titrators - PA/PH/OMCL (07) 108 R11, 2022.

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