BENCHMARK TEST

VOLUMETRY: HYDRANAL™ VS. REAGENT M

Honeywell

INTRODUCTION

Because of its selectivity and accuracy, Karl Fischer (KF) titration is the method of choice when determining water content.

For reliable results and to reduce laboratory costs in volumetry, the most popular KF technique, negative effects like reagent crystallization must be minimized.

Water content or contamination is a cause for major concern in a large number of applications. Several methods are available to determine water content. A Karl Fischer (KF) volumetric titration is one of the most popular methods that allows the addition of various solvents and enables water determination across a wide range of samples.

In volumetric titration, iodine present in a titrating agent (titrant) is directly added to the sample in the titration cell via a burette. The iodine reacts with the water present in the sample according to the Karl Fischer reaction:

$CH_3OH + SO_2 + RN \leftrightarrow [RNH]SO_3CH_3$

$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2\ [RNH]I$

As soon as no water is available, a small excess of iodine arises, which is recognized as the end point of the titration. Since the amount of titrated water is proportional to the total amount of iodine added, the water content can be determined from the consumption of the titrant containing a known amount of iodine. To support various sample requirements titrants contain different amounts of iodine resulting in different titer values (1, 2 or 5).

Nowadays, KF titrators are equipped with modern burettes (dosing units) which are electronically controlled to dose the titrant with high precision. Some burette tubes are additionally equipped with anti-diffusion valves preventing uncontrolled leakage. Titrant crystallization can permanently damage these tubes and valves if left unchecked, leading to costly replacements (see Fig. 1 and Fig. 2).

One component titrants are most impacted by crystallization since all substrates needed for the KF reaction are placed in the same bottle. The rate of crystallization is strongly influenced by humidity, however by choosing the right brand, crystallization can be significantly delayed and highly reduced.

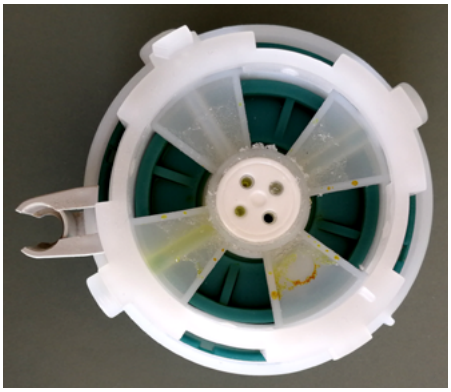

Fig. 1. *Example of dosing unit contaminated with crystals.*

Fig. 2. *Example of dosing tube contaminated with crystals.*

COMPARISON TESTS: CRYSTALLIZATION

Crystallization tests have been performed on Hydranal™ and Reagent M one-component titrating agents with titer 1, 2, 5, and 5 for ketones (5 K/5 Keto).

In practice, crystallization takes place if iodine in the titrant is consumed due to contact with humid air (possible through water migration into the plastic tubes when the titrant is not moved/kept attached to the titrator for a long time) or if the solvent from the titrant evaporates (possible via burette's dosing tube tips when dry stored or through valves due to capillary effect). These effects were simulated under accelarated conditions[1] to monitor crystallization in Hydranal and Reagent M.

100 mL of each titrant, Hydranal and Reagent M, was neutralized by adding ultrapure water until the color of the titrant changed from dark brown to yellow-orange. 8 mL of each of the neutralized titrants was transferred via a syringe into separate 10 mL glass vials, placed inside a fume hood and observed daily. Relative humidity in the lab was 30% +/- 5%.

To simulate the physical movement of the titrant[2], some drops of the upper part of the liquid where moved to the screw part of the vial on a daily basis.

Regardless of titer value, Reagent M began to crystallize within a few days. Hydranal on the other hand, did not start crystallization until 2 weeks after the test was started (see Table 1).

All tests were carried out and approved by the Hydranal Center of Excellence in Seelze, Germany.

Table 1. Comparison of crystallization start time for different titer values of Reagent M and Hydranal.

REAGENT M	START OF CRYSTALLIZATION
Titer 5 Keto	1 day
Titer 5	2 days
Titer 2	3 days
Titer 1	5 days

HYDRANAL	START OF CRYSTALLIZATION
Composite 5 K	14 days
Composite 5	14 days
Composite 2	14 days
Composite 1	14 days

REAGENTS TITER 5 FOR KETONES:

Day 1: *Reagent M crystallization starts*

Day 14: *Hydranal crystallization starts*

REAGENTS TITER 5:

Day 2: *Reagent M crystallization starts*

Day 14: *Hydranal crystallization starts*

Left to right:
Hydranal-Composite 5 K (left) and Reagent M Titer 5 Keto (right) after 1 day;

Hydranal-Composite 5 K (left) and Reagent M Titer 5 Keto (right) after 14 days;

Hydranal-Composite 5 (left) and Reagent M Titer 5 (right) after 2 days;

Hydranal-Composite 5 (left) and Reagent M Titer 5 (right) after 14 days.

REAGENTS TITER 2:

Day 3: *Reagent M crystallization starts*

Day 14: *Hydranal crystallization starts*

REAGENTS TITER 1:

Day 5: *Reagent M crystallization starts*

Day 14: *Hydranal crystallization starts*

Left to right:
Hydranal-Composite 2 (left) and Reagent M Titer 2 (right) after 3 days;

Hydranal-Composite 2 (left) and Reagent M Titer 2 (right) after 14 days;

Hydranal-Composite 1 (left) and Reagent M Titer 1 (right) after 5 days;

Hydranal-Composite 1 (left) and Reagent M Titer 1 (right) after 14 days.

1. titrants were kept in open vials instead of connecting to the instrument; results can be extrapolated to normal conditions;
2. typically, titrants are exposed to mechanic stress by moving parts inside a dosing unit of a titration device;

CONCLUSION

Reagent M was found to crystallize much faster and more prominently than Hydranal within a few days of starting the test. Such crystals, if formed inside the dosing units and dosing tubes, can seriously damage critical parts of the titrator, resulting in costly replacements.

Using reagents that delay and reduce crystallization not only prevents additional cleaning but also costly service and replacement of damaged titration equipment.

Reagent M was found to crystallize rapidly even in a humidity controlled environment. Hydranal on the other hand did not crystallize until much longer and the amount of crystallization was visibly low in comparison with Reagent M. This ensures quick and easy cleaning of the titration cell and saves valuable working time and cost. Hydranal fulfills the requirements for an ideally functioning KF reagent.

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