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HYDRANAL™ Technical Information Sheet T001

Determining the Titer of Karl Fischer Reagents and Influences on Accuracy

For the correct calculation of the water content, the current titer (water equivalent) of the reagent used must be known. The titer states how much reagent is required in mL in order to titrate exactly 1 mg water. The indication of the titer is given in mg water per mL reagent (example: titer = 5.125 mg/mL).

The titer determination is carried out by presenting a known quantity of water in the titration vessel and determining the reagent volume required for that.

Pure water may be used. However, the quantities to be used are extremely small. For example, to determine a reagent with titer 2, depending on the size of the burette, only 10-15 mg or for titer 5 only 20-40 mg water is needed. In extreme cases (for titer 1) only 5-10 mg are required. These small quantities often cause very fluctuating results due to handling and weighing inaccuracies.

ISO 760 specifies the use of sodium tartrate dihydrate for titer determination. The theoretical water content of this substance is 15.66%. Therefor a correspondingly larger sample size can be selected (e.g. 150-200 mg for titer 5), which significantly reduces weighing errors. The limited solubility in methanol is a disadvantage (approx. 100 mg / 30 mL). This requires a new filling of the titration cell for each individual determination. The titer determination is only carried out correctly if the standard is clearly dissolved at the end of the titration. The addition of Hydranal-Solvent improves the solubility.

For many working media, liquid standards must be used because, for example, in reagents containing ethanol or in the special reagents like Hydranal-Working Medium K or Hydranal-Medium K, sodium tartrate dihydrate is almost insoluble. If sodium tartrate dihydrate cannot be replaced by liquid standards, it is recommended to use Hydranal-Solvent or a mixture of methanol and Hydranal-Solvent for better solubility. After the titer has been determined, a switch is made back to the special reagent required for sample determination.

Liquid standards offer the simplest and quickest titer determination. If, for example, Hydranal-Water Standard 10.0 is used, a triple determination can be carried out from one ampoule of standard without replacing the filling of the titration vessel. The standard contains 10 mg of water per gram. The batch-specific water content is stated on the enclosed certificate. This standard ensures a high level of reliability, as it is protected from external influences through the filling and storage in ampoules.

Suitable Water Standards (tested against NIST SRM 2890):
34849 HYDRANAL-Water Standard 10.0
34425 HYDRANAL-CRM Water Standard 10.0
34696 HYDRANAL-Standard Sodium Tartrate Dihydrate
34424 HYDRANAL-CRM Sodium Tartrate Dihydrate

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Influence of different media on the titer

The titer of a KF titration medium is identical in combination with all of the Hydranal KF media. With these media, the accuracy of the stoichiometry of the KF reaction is guaranteed. For example, if the titer of Hydranal-Composite is determined in methanol, it does not need to be re-determined when the titration medium is switched to Hydranal-Medium K. This statement remains valid if the Hydranal reagent for the titration vessel is used in its original quality. Additions of external solvents are only possible in limited amounts.

Recommendation for the acceptability range for the standard deviation of the titer determination

A double determination should be performed as a minimum. A triple determination allows for the elimination of any possible outliers. With a fivefold (or higher) determination the results provide a statistically representative mean value. Deviations in the second decimal place are typical.

An RSA (relative standard deviation) of ≤0.2% is generally achievable. This would be consistent with individual values of, for example: 5.33 / 5.34 / 5.35 / 5.36 / 5.35 with MV (mean value) = 5.346 and RSA = 0.21%. Standard deviations of >0.4% should be regarded critically. This would be consistent with individual values of, for example: 5.33 / 5.38 / 5.35 / 5.36 / 5.32 with MV = 5.348 and RSA = 0.45%. With a double determination, the example values 5.32 / 5.38 would produce a significantly higher RSA of 0.79%. The recommended acceptable level would be significantly exceeded here.

Influence of the environment on the titer

The Hydranal reagents are extremely stable in the closed bottle. During the use of the reagents, penetrating humidity is absorbed. The KF reaction takes place and iodine is consumed according to the water quantity, which causes a titer decline. 1 L of air contains on average 12-15 mg of water. The influence of air ingress can be very significant.

To protect the reagent it is important, therefore, to fit a drying tube to the connected reagent bottle. A molecular sieve 0.3 nm or humidity absorber with indicator is well-suited as a drying agent. The replacement of the molecular sieve every six weeks is recommended, if using a humidity absorber no later than when the indicator changes color. Molecular sieve can be regenerated at 300°C (min. 4 h). Additional apply of a dry airflow or a vacuum can improve the result of the regeneration process. 140°C is sufficient for the humidity absorber. The colour intensity indicates the level of dryness.

Suitable drying agents:
34241 HYDRANAL-Molecular Sieve 0.3 nm
34788 HYDRANAL-Humidity Absorber

In case of (virtual) stoppage of the titrator overnight, water is absorbed into the plastic tubes and the titer of the reagent contained therein no longer matches the titer of the supply bottle. Thorough flushing is recommended the following morning.

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CAUTION! Temperature changes also have an impact on the titer. If the reagent heats up by 1°C, the titer decreases by 0.1% due to the volume expansion. This should be taken into account in the event of strong temperature fluctuations during the work day.

Influence of decomposition on the titer

As pure alcoholic iodine solutions, the titration media of the two-component systems (Titrant/Solvent) are very titer stable. The one-component reagent, Hydranal Composite, however, with its complex composition is subject to a weak "decomposition", which can vary somewhat depending on the storage conditions. At a slightly elevated room temperature, the maximum decline is around 5% per year. This corresponds to max. 0.1% per week, and is therefore negligible in the weekly routine.

Recommendation for the acceptable range of the titer decline

All of the described effects show that the titer can slowly decline over longer storage periods or periods of use. Many users of the KF titration are uncertain as to the extent to which a modified titer can still be accepted. The question arises as to how long a reagent may be used. The fact is that in the case of regular titer determinations (i.e. if the current titer is known), the calculation of the water content can be carried out without errors. With a low titer, correspondingly more reagent is used for titration and the analytical results are still correct.

Recommendations for acceptable titer decline:

- for reagent titer 5 mg/mL: titer decline up to 3.5 mg/mL is acceptable
- for reagent titer 2 mg/mL: titer decline up to 1.4 mg/mL is acceptable
- for reagent titer 1 mg/mL: titer decline up to 0.6 mg/mL is acceptable

Influence of the titration cell on titration behaviour

The state of the titration cell has a major influence on the titration behaviour. A titration cell is never completely closed, so there is always a certain amount of moisture in the headspace of the cell. If this moisture is absorbed by the media, it causes a consumption of reagent. This consumption, which is not linked to the water of the sample, is indicated as the drift. After the titration is completed, the reagent consumption should not be higher than 0.01 mL per minute (10 µL/min).

Recommendations for maximum acceptable drift values:

- with reagent titer 5 mg/mL: 50 µg water/min, equivalent to consumption 10 µL/min
- with reagent titer 2 mg/mL: 20 µg water/min, equivalent to consumption 10 µL/min
- with reagent titer 1 mg/mL: 10 µg water/min, equivalent to consumption 10 µL/min

The smaller the titer of the reagent used, the higher the influence of the penetrating moisture. It is therefore extremely important, in particular when using low titers, that the background moisture of the cell is very low. If this is not the case, it will be difficult for the system to find an endpoint. Ultimately, sluggish endpoints produce falsified, higher water content results.

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Therefore, it is recommended to regularly check sealing rings and septa, to dry openings with a paper towel before use, to refill drying tubes regularly and to give the cell sufficient time for the pre-titration in order to achieve a low and stable drift. Good preparation helps prevent subsequent time-consuming problems.

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