

## HYDRANAL®-Water Standards

### Introduction

Calibration, validation and control of analytical instruments and reagents is a central requirement in regular Quality Management systems. In the case of Karl Fischer titrations, the most widely used method for water determination, a known amount of water is required. Pure water can be used, but the amounts needed (10 mg for volumetry, and 100 µg – 1 mg for coulometry) are difficult to weigh.

We recommend using water standards with an exact confirmed water content

- for titre determination
- for monitoring precision and accuracy
- for validation and inspection of KF titrators according to ISO 9000 and GLP guidelines

Traceability to a national standard or to a SI unit is often required in these guidelines.

Two of our HYDRANAL®-Water Standards, one for volumetry and one for coulometry, respectively, are traceable to the NIST standard reference material SRM 2890, Water Saturated Octanol. «NIST» stands for the National Institute of Standards and Technology of the USA.



### Water Standards

Liquid HYDRANAL®-Water Standards are currently used for the volumetric titre determination of Karl-Fischer reagents, to control coulometric instruments and, most importantly, for the quality control of Karl-Fischer instruments in general as it relates to ISO 9001-9003 and other standard procedures.

Three different water standards are currently available. Liquid HYDRANAL®-Water Standards consist of a solvent mixture with specific composition and a precisely determined water content. The exact water amount can be found on a Certificate of Analysis which is enclosed in each product package, (figure 1).

HYDRANAL®-Water Standards are sealed under Argon in 4 ml or 8 ml glass ampoules. The humidity-proof packaging allows for storage up to five years. Each box contains 10 ampoules.



Figure 1: HYDRANAL®-Water Standards sealed glass ampoules under Argon. The Certificate of Analysis is included in the pack.

### Contents:

- **Standards for Karl Fischer Titration**
- **Titre Determination of Volumetric Reagents**
- **Result Control of Coulometric Instruments**
- **Instrument Validation according to ISO 9000 and related Guidelines**

### General Instructions for Use

Opening each ampoule just before a measurement will reduce the risk of atmospheric moisture entering the ampoule and falsifying results (depends on local humidity conditions). It is recommended that only glass syringes be used since most plastic syringes can store or release a certain amount of water over time. It is common practice to flush each syringe initially with approximately 1 ml of HYDRANAL®-Water Standard and eventually to draw the whole remaining volume into the syringe. This will reduce exposure of the standard to atmospheric moisture.

### 34849 HYDRANAL®-Water Standard 10.0

Standard for volumetric Karl Fischer titration.

This standard is traceable to NIST SRM 2890.

The following instructions are recommended for the titre determination of the Karl Fischer reagent.

### Titre Determination of Volumetric Karl-Fischer Reagents

1. Prepare the instrument in the usual way (charge system with Karl Fischer reagent and select the titration parameters).
2. Add the solvent combination, or HYDRANAL®-Solvent, into the cell and titrate content to dryness (pretitration step).
3. Break open an ampoule at the white ring marking the score on the neck.
4. Use a glass syringe and draw 1 to 2 ml of standard (equals 10 to 20 mg water). Weigh and add standard into the titration cell.
5. Perform the titration and repeat this process one to two more times.

Figure 2:  
Liquid Water Standards with a Certificate of Analysis and defined Water Content. Solid Standard permitting Functional Tests using the KF Oven.

### 34849 HYDRANAL®-Water Standard 10.0

- with 10 mg water per gram (10,000 ppm)
- for volumetric Karl Fischer titration, 10 x 8 ml

### 34828 HYDRANAL®-Water Standard 1.00

- with 1.0 mg water per gram (1,000 ppm)
- for general coulometric KF titration, 10 x 4 ml

### 34847 HYDRANAL®-Water Standard 0.10

- with 0.1 mg water per gram (100 ppm)
- for coulometric titration of small absolute amounts of water, 10 x 4 ml

### 34748 HYDRANAL®-Water Standard KF-Oven

- for the control of KF ovens using coulometric and volumetric water determination, 10 g

6. Calculate your results using the following formula:

$$T = \frac{E \times W}{Vol}$$

- T = Titre (in mg water per ml)  
E = Weight of HYDRANAL®-Water Standard (in g)  
W = Water content of HYDRANAL®-Water Standard from the enclosed Certificate of Analysis (in mg/g)  
Vol = Volume of consumed KF reagent (in ml)

Plastic tubing found on almost all KF instruments may not be impervious to water and may cause a variation of titre within the delivery system. To avoid errors in precision and accuracy, flush the KF burette and the plastic tubing thoroughly before running a titre determination.

### 34828 HYDRANAL®-Water Standard 1.00

Standards for general coulometric KF titration. This standard is also traceable to NIST SRM 2890. Although coulometry is thought of as an «absolute» method, not all titrated values are necessarily correct. Air humidity, electrode poisoning, or sample matrix conditions can influence the results. It is therefore necessary to test the system with known water quantities and to check the recovery data. The validation of the instrument should typically be performed once the titration vessel has been charged with the appropriate reagents. To monitor for interferences caused by the sample matrix a control test could be undertaken immediately after a sample was analysed. In each case the theoretically added amount of water should correspond to the experimentally titrated amount of water.

### Instructions for Validation and Control of Coulometric Measurements

1. Turn on the instrument and wait until the cell is dry.
2. Break open an ampoule at the white ring marking the score on the neck.
3. Rinse the syringe with approximately 1 ml HYDRANAL®-Water Standard 1.00.
4. Draw the rest of the standard into the syringe.
5. Start the analytical determination and inject a measured amount (determine the exact mass by weighing).
6. Repeat the determination one to two more times.

Calculate the amount of water from the specified value on the test certificate and compare it with the result obtained experimentally. Our recommendation is with 1,000 µg water the deviation should not exceed 50 µg (30 µg is preferred). When the difference is greater, the source of the error should be determined. Other individual limits can be set by the user.

### **34847 HYDRANAL®-Water Standard 0.10**

Standard for coulometric titration of small absolute amounts of water.

#### **Validation and Control of Coulometric Measurements**

This water standard should be used for coulometric quality control. It is typically recommended when the water amount of the sample is small and around 100 µg per gram of sample. However, this standard requires excellent technique and skillful handling to prohibit extraneous sources of moisture from affecting the reliability of the measurement. If care is not properly exercised in handling this standard or, in general, low moisture containing samples, the titrated values will always be too high.

#### **Control of the Karl Fischer Instruments with Reference to ISO 9000 and GLP Guidelines using the a/m Standards**

Karl Fischer titrations are used to determine product quality by measuring water content. The quality assurance program to be used to ensure adequate control of this analytical method must include the following:

1. The analytical protocol must be clearly written and verified.
2. All results pertaining to the analytical protocol must be documented
3. The KF titrator must be checked at regular intervals for accuracy and precision, and the results must be documented.

HYDRANAL®-Water Standards can be used to check, control and validate Karl Fischer instruments since the water content is analysed using two independent methods. A certificate of analysis is included in each pack. The traceability is also confirmed on this certificate.

The international guidelines give only general recommendations and not precise work instructions. To solve this problem, we have developed documentation for analytical procedures and instrument validation. These procedures are available free of charge. Please request our publication entitled, «ISO 9000 and Karl Fischer Titration» from our Karl Fischer technical center. Please refer to the last page of this publication for the address and phone number.

### **34748 HYDRANAL®-Water Standard Karl-Fischer-Oven**

Standards for the control of KF ovens using coulometric and volumetric water determination. This solid standard contains 5.55 % water as water of crystallization. The exact value of every lot can be found in the enclosed Certificate of Analysis. The standard can be used to check the whole apparatus. If the water content found differs from the value in the certificate, the function of the connected volumetric or coulometric KF titrator should be checked using liquid HYDRANAL®-Water Standards.

We recommend the following procedure:

1. The coulometric or volumetric cell is titrated to dryness according to the manufacturer's instructions.
2. The KF oven is heated to 220°C and the carrier gas (air, Argon) is dried over a molecular sieve before being connected into the cell until a low and stable drift is achieved.
3. An extraction time of 300 seconds is set on the KF oven.
4. 100 mg of standard for the coulometric control, or 300 mg for the volumetric control, are weighed accurately into the sample boat. The boat is introduced into the hot zone of the oven.
5. Nearly all modern KF titrators calculate the water content automatically after the input of the sample weight. The water content can also be calculated according to the typical calculation procedures.

If the results are not satisfactory, the single coulometric or volumetric instrument has to be checked as described in the sections above. This is necessary to determine if the fault is caused by the KF oven or the KF instrument.

#### **HYDRANAL® Technical Help**

Karl-Fischer-Titration requires not only high performance reagents and instrumentation but also specific theoretical and practical knowledge not often found in college or industrial training programs. Additionally, existing applications or measurement protocols are often outdated since they were simply passed on over the years without the necessary revisions or changes. To provide analysts around the world with the most up-to-date and product specific information possible we have established a Karl Fischer help line which can be consulted free of charge. Please feel free to contact. Please refer to the last page of this publication for the address and phone number.

## Over 20 Years Experience in Karl Fischer Titration

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