Automated sample measurement in Karl Fischer titration

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Karl Fischer

Summary

Karl Fischer titration is not the labor-intensive method of the past, but an easily automated with standard instrumentation. As shown by these examples, Karl Fischer titration remains a readily automated technique for directly and selectively analyzing the moisture content of disparate substances. Volumetric Karl Fischer titrations require regular titer determinations, as reagent manufacturers only provide approximate titers that change with time. These titer determinations are laborious, especially when performed manually. A completely automated procedure using a capillary, a Metrohm automatic burette (Dosino), and ***tiamo***™ software takes over this laborious task. Results were confirmed by manual titer determinations.

Automated sample measurement is excellent for determining the water content in highly viscous compounds. The exact dosing of small volumes with Metrohm's unique dosing technology compensates with the high water contents of two industrial water-glycols studied. When combined with coulometric Karl Fischer titration instead of volumetric Karl Fischer titration, the automated procedure excels at the analysis of low-molecular-weight hydrocarbons such as n-pentane. Lastly, automated sample measurement is a powerful technique to automate a labor-intensive and human error-prone suitability test for volumetric Karl Fischer titration required in chapter 2.5.12 of the European Pharmacopoeia.

Introduction

Karl Fischer titration is a highly effective method for determining the water content in various matrices. It is performed in closed titration vessels to prevent contamination due to atmospheric moisture. Liquid samples are injected into a Karl Fischer titration cell through a septum with a syringe and a needle. The quantity of sample added is determined by either volume or weight. Compared with automated sample measurement, manual testing is associated with some disadvantages. In terms of safety at work, the use of syringes and needles poses a risk of injury to the user.

For samples with a high water content (> 40%), Karl Fischer titration requires only a few milligrams of sample material per determination. In these cases, only very experienced users are typically able to achieve the high level of precision and accuracy that is offered by automation.

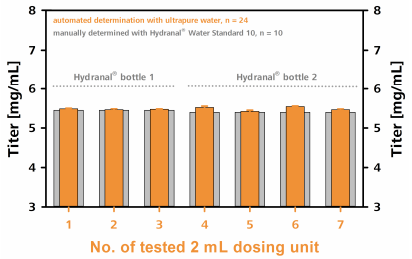
Using four examples, we describe a method for automated and precise dosing of liquid samples into the Karl Fischer titration cell using Metrohm Dosino liquid handling technology. This revolutionary and proven technology saves the user time and money by the accurate and precise handling of volumes down to the low microliter level.

System setup

- 901 Titrando
- 815 Robotic USB Sample Processor XL

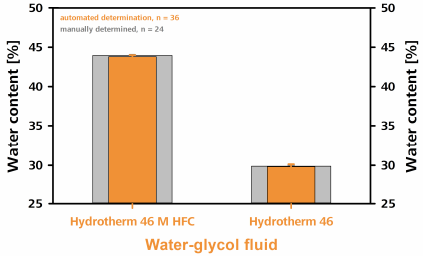
Automated titer determination

Manufacturers only offer Karl Fischer reagents that have approximate titers that change with time. Ultrapure water, however, is an excellent standard for titer determination, but requires precise dosing volumes. By using a capillary, a Dosino, and ***tiamo***™ software or, alternatively, the 900 Touch Control, accurate and automated titer determinations with water are possible. The titer was automatically determined with ultrapure water using seven 2 mL dosing units. The results were compared to those obtained manually using the Hydranal® Water Standard 10. With a minimum of labor and consumables in a minimum amount of time, automated titer determination achieves recoveries between 97 and 100% and relative standard deviations below 0.3%.



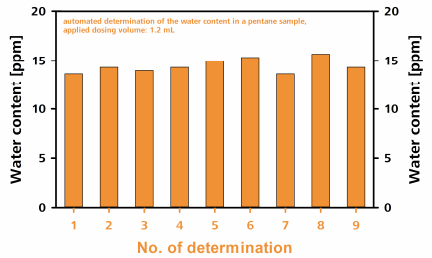
Water content in highly viscous compounds

Water-glycol fluids have excellent lubrication, environmental, and fire-resistant properties. While high-molecular-weight polyglycols provide the necessary viscosity, high water contents (up to 45%) ensure fire resistance. The above described procedure, which was used for the automated determining of the titer, is ideally suited to control the fluid`s glycol/water ratio. Besides the labor-saving procedure, the method stands out for its capacity to exactly dose very small fluid aliquots. This significantly lowers titrant and solvent consumption without affecting precision and accuracy. The fully automated procedure was applied to two industrial glycol-water fluids, one being a HFC (hydraulic force control) fluid. The results of the labor-prone manual water determination are shown for comparison.



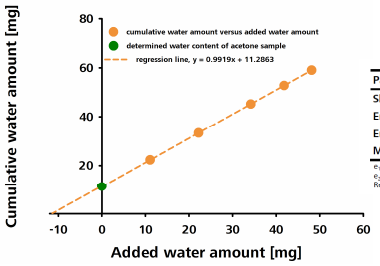
Water content in low-boiling organic solvents

In preparative organic chemistry, water-free solvents are required. Water traces promote unwanted side reactions such as hydrolysis, polymerization, and racemization. The presence of water also promotes corrosion and microbial contamination. Because the water content in nonpolar organic solvents is low, coulometric Karl Fischer titration is used instead of the volumetric Karl Fischer technique used in the other examples in this poster. The procedure was tested for n-pentane. Because of its low viscosity and surface tension, n-pentane is extremely difficult to pipette. Automated sample measurement with capillary injection using a 5 mL dosing unit overcomes this problem and allows a precise determination of the water content.



Suitability test according to Ph. Eur.

Since 2008, the European Pharmacopoeia (Ph. Eur.) requires a suitability test (chapter 2.5.12) for the volumetric Karl Fischer titration. The laborious procedure validates if the selected titrant/solvent system is suitable for a precise water determination in the substance to be examined. To this end, the water content of the substance is first determined. Afterwards, known amounts of ultrapure water are sequentially added (at least 5) and determined. From the regression line, slope, axis intercepts, and percentage mean recovery are calculated. The example shows the suitability test for acetone. According to the regression data, the chosen titrant/solvent system complies with all the requirements of the Ph. Eur. The automated procedure takes over the six determinations, calculates the results, and provides a well-arranged report.



Parameter	Requirement Ph. Eur.	Achieved	Result
Slope	0.975…1.025	0.9919	+
Error e_1	+2.5…−2.5%	0.39%	+
Error e_2	+2.5…−2.5%	1.21%	+
Mean recovery	97.5…102.5%	99.28%	+

e_1 = 100 × [(a-M)/M]; a = y-axis intercept, M = compound's water content
e_2 = 100 × [(d-M)/M]; d = x-axis intercept, M = compound's water content
Recovery = 100 x cumulative water amount/added water amount

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