

THE KARL FISCHER TITRATION OF WATER

Kenneth A. Connors

School of Pharmacy

University of Wisconsin

Madison, Wisconsin 53706

Abstract. The Karl Fischer method for the determination of water is briefly reviewed. The chemistry of the reaction of Karl Fischer reagent with water is discussed, and modifications in the reagent composition are summarized. Some of these modifications result in more stable reagents. The visual, spectrophotometric, and electrometric forms of the Karl Fischer titration are described and compared.

INTRODUCTION

In 1935 Fischer (1) described a titrimetric method specific for water. The titrant, which is now known as the Karl Fischer reagent, is a solution of iodine, sulfur dioxide, and pyridine in

1891

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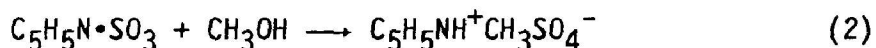
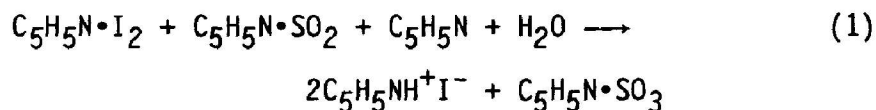
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methanol. In the half-century since its introduction, the Karl Fischer titration has become a standard procedure for the determination of water in many types of samples. The subject has been repeatedly reviewed, most notably in a 1980 book, by Mitchell and Smith, devoted solely to this technique (2). This exhaustive treatment by Mitchell and Smith should be consulted for a comprehensive survey of the literature on the analytical chemistry and applications of the Karl Fischer titration. The present review has the more limited aim of briefly describing the chemical basis of the method and of citing some recent work on modifications that may be of interest to the potential user of the Karl Fischer titration.

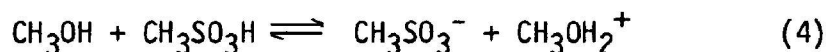
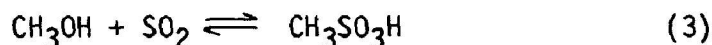
CHEMISTRY

The reaction of water with the Karl Fischer reagent is commonly written as this 2-step process:

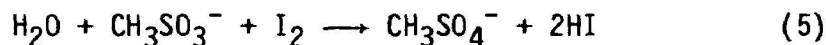


The species $\text{C}_5\text{H}_5\text{N}\cdot\text{I}_2$, $\text{C}_5\text{H}_5\text{N}\cdot\text{SO}_2$, and $\text{C}_5\text{H}_5\text{N}\cdot\text{SO}_3$ may be charge-transfer complexes, and $\text{C}_5\text{H}_5\text{NH}^+\text{I}^-$ and $\text{C}_5\text{H}_5\text{NH}^+\text{CH}_3\text{SO}_4^-$ are salts. The chemistry of the system is certainly more complicated than

indicated by these two reactions, however, as demonstrated by the observation that the water titer of Karl Fischer reagent gradually decreases even in the absence of water, presumably due to the occurrence of side-reactions. Many products have been isolated from spent (i.e., exhausted) Karl Fischer reagent. (Surprisingly, chromatography does not yet seem to have been applied to the chemistry of this system in a detailed way, and this appears to be a promising area for further research). Kinetic studies show that the rate of loss of iodine is first-order each in iodine, in sulfur dioxide, and in water. The reagent also contains the triiodide ion I_3^- , formed in an equilibrium between iodine and iodide, and monomethyl sulfite, formed as follows:



The pH-rate behavior indicates that $CH_3SO_3^-$ is the actual reactant in the redox reaction with water and iodine, as shown in Eq. (5).



It is believed that pyridine serves as a buffer, maintaining the effective pH in a range so as to generate the reactive conjugate base, $CH_3SO_3^-$.

According to Eqs. (1) and (2), the stoichiometric ratios of the reactants are $1\text{I}_2:1\text{SO}_2:1\text{CH}_3\text{OH}:3\text{C}_5\text{H}_5\text{N}$, but the subsequent equations, as well as the existence of side reactions, result in depletion of some reactants, and the reagent is prepared so that the iodine is the limiting ingredient, a composition of $1\text{I}_2:3\text{SO}_2:10\text{C}_5\text{H}_5\text{N}$ dissolved in excess methanol being typical. The titer of Karl Fischer reagent is expressed as milligrams of water per milliliter of reagent. Typical titers are 3 to 6 mg $\text{H}_2\text{O}/\text{ml}$ reagent for macroscale titrations, and a tenth of this for titrations on the microscale. Freshly prepared Karl Fischer reagent has a strength of about 80% of the theoretical, but this falls rapidly in the first 24-48 hours, so some authors advise that the reagent be prepared at least a day prior to its use. Methanol usually serves as the solvent for the titration sample.

Many modifications of the standard composition have been proposed, most of these changes being replacements of the pyridine or the methanol. Karl Fischer titrant prepared with methyl cellosolve (2-methoxyethanol) is more stable (3) than the usual reagent containing methanol. Dimethylformamide (DMF) is also an effective replacement for methanol (4), though electrometric end point detection is required because the color change is not sharp.

Replacement of the pyridine by other bases is an attractive possibility because of the unpleasant odor of pyridine. Some of the resulting reagents are so-called "one-component" reagents,

that is, reagents containing the I_2 , SO_2 and base all in one titrant solution; "two-component" formulas typically consist of the solvent, which is a solution of SO_2 and the base in methanol or other medium, and the titrant, consisting of iodine dissolved in methanol. The sample is dissolved in the solvent component, and this is titrated with the titrant component. For example, a typical two-component formula consists of sulfur dioxide and sodium acetate in methanol as the solvent, and iodine in methanol as the titrant. The standard composition can be used in the same way, SO_2 and pyridine dissolved in methanol being the solvent and iodine in methanol the titrant. Scholz has developed both one-component and two-component reagents in which pyridine is replaced with diethanolamine (5-7); 2-methoxyethanol is the solvent in the one-component solution, and methanol is the solvent for the two-component formulas. An unusual reagent is composed of urea, sodium salicylate, and sulfur dioxide in methanol (the solvent component) and iodine in methanol (the titrant) (8).

Blomgren and Jenner (9) developed a Karl Fischer reagent with pyridine in which iodide was added to establish the ratio $I^-/I_2=3.2$. This composition gives a very stable reagent, even with methanol as the solvent. Two methods of preparation are described; in one of these the iodide is added as pyridinium iodide, $C_6H_5NH^+I^-$, and in the other it is generated in situ by the addition of a calculated amount of water.

Few analysts will choose to prepare their own Karl Fischer reagent. Several versions are commercially available, including

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