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THE KARL FISCHER TITRATION OF WATER

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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 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:

$$C_5H_5N{\bullet}I_2 + C_5H_5N{\bullet}SO_2 + C_5H_5N + H_2O \longrightarrow 2C_5H_5NH^+I^- + C_5H_5N{\bullet}SO_3 \qquad (1)$$

$$C_5H_5N{\bullet}SO_3 + CH_3OH \longrightarrow C_5H_5NH^+CH_3SO_4^- \qquad (2)$$

The species $C_5H_5N{\bullet}I_2$, $C_5H_5N{\bullet}SO_2$, and $C_5H_5N{\bullet}SO_3$ may be charge-transfer complexes, and $C_5H_5NH^+I^-$ and $C_5H_5NH^+CH_3SO_4^-$ 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:

$$CH_3OH + SO_2 \rightleftharpoons CH_3SO_3H \qquad (3)$$

$$CH_3OH + CH_3SO_3H \rightleftharpoons CH_3SO_3^- + CH_3OH_2^+ \qquad (4)$$

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).

$$H_2O + CH_3SO_3^- + I_2 \longrightarrow CH_3SO_4^- + 2HI \qquad (5)$$

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

COMPOSITION OF THE REAGENT

According to Eqs. (1) and (2), the stoichiometric ratios of the reactants are $1I_2:1SO_2:1CH_3OH:3C_5H_5N$, 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 $1I_2:3SO_2:10C_5H_5N$ 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 H_2O/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 one-component and two-component formulas, pyridine-free reagents, and stabilized reagents. The compositions of these products are not usually specified. "Stabilized" reagents may be prepared with 2-methoxyethanol instead of methanol, or they may be made up to the I^-/I_2 ratio given by Blomgren and Jenner (9). The Hydranal® reagents are based on Scholz's formulas (5-7).

In the coulometric titration method, the iodine is generated by oxidation of iodide.

$$2I^- \longrightarrow I_2 + 2e \qquad (6)$$

This is done in the presence of the other ingredients of the Karl Fischer reagent. The coulometric reagent therefore must contain iodide but no iodine, and even spent Karl Fischer reagent has been used. Since one molecule of water corresponds to one molecule of iodine (Eq. 5), which is equivalent to two electrons, 2F coulombs corresponds to 18.0 g of water, or 1 mg H_2O is equivalent to 10.71 coulombs.

STANDARDIZATION OF THE TITRANT

Liquid water is an obvious primary standard for the standardization of Karl Fischer reagent. Its disadvantages are its liquid state and its low molecular weight. Samples of water can be weighed out, or can be delivered by volume and the weight calculated from the density.

More commonly a solution of water is quantitatively prepared in methanol, and aliquots of this solution are taken for titration. This method has the advantage that a substantial sample of water is weighed (typically 10 to 15 g of H_2O per liter of methanolic solution). It is essential that the same lot of methanol be used for the preparation of this standard solution and for blank titrations of the methanol to correct for traces of water in the methanol. n-Propyl alcohol has been recommended as the solvent because it is less volatile and less hygroscopic than methanol (10).

Stable salt hydrates constitute another class of primary standard. Many of these have been studied, but only two have found wide use. One of these is sodium acetate trihydrate (theoretical water content 39.72%). This salt is soluble in methanol, but questions have been raised about the constancy of the water content.

By far the most popular primary standard has been sodium tartrate dihydrate, $Na_2C_4H_4O_6 \cdot 2H_2O$ (theoretical water content 15.66%). Sodium tartrate dihydrate appears to be non-hygroscopic and quite stable under ordinary storage conditions. Its main drawback as a primary standard is its limited solubility in methanol, which does not generate confidence that all of its water of crystallization is released during the titration. Bryan and Rao (11) have made a careful study of the suitability of sodium tartrate dihydrate as the primary standard for Karl Fischer titration. They studied samples of sodium tartrate dihydrate from five commercial sources, obtaining concordant results. Drying the samples to constant weight yielded an actual average water content of 15.61%, or about 0.3% less than the theoretical. They make these recommendations for the most accurate work:

1. The actual water content should be determined by drying to constant weight.
2. The titration should be carried out slowly so that all of the water of crystallization is released prior to the end point.
3. The buret and titration assembly should be made with glass or stainless steel tubing, because rubber or plastic tubing is permeable to water vapor.
4. Titration vessels should be purged with dry carbon dioxide rather than nitrogen.
5. The buret and titration assembly should be protected from atmospheric moisture with phosphorus pentoxide adsorbent rather than calcium sulfate or magnesium perchlorate.

END POINT DETECTION

Visual Titration. Active Karl Fischer reagent has the reddish-brown color characteristic of iodine, whereas spent Karl Fischer reagent is yellow. It is therefore possible to carry out Karl Fischer titrations (in either the direct or the back-titration mode) with visual detection of the end point, the reagent serving as the indicator. These titrations are most successful on the macro scale with full-strength Karl Fischer reagent. (Reagent prepared with DMF as the solvent tends to yield a poor visual end point and should not be used in this way).

Because of the simplicity and low cost of the visual titration method, it is recommended for occasional use or for preliminary studies to establish feasibility. The only unusual precaution to be observed is protection from contamination by atmospheric moisture. Volumetric flasks are useful titration vessels because of their long necks, which restrict access by the atmosphere. Titration precision can be improved by titrating all solvent blanks, standardizations, and unknown samples to match the same reference color, which is maintained in a stoppered volumetric flask. Simple directions have been published (12).

Spectrophotometric Titration. Several instrumental methods make use of the difference in color of active and spent Karl Fischer reagent. Perhaps the simplest of these is a spectrophotometric titration in which the absorbance of the titration solution is measured as a function of titrant volume (13). In a direct titration with Karl Fischer reagent the absorbance before the end point is low and nearly constant; after the end point the absorbance rises in accordance with Beer's law. The intersection of the straight lines marks the end point. Since the Karl Fischer reagent has an absorption spectrum showing rising absorption toward the shorter wavelength end of the visible region, without an absorption maximum, the choice of wavelength is not critical, and 525 nm was used in the original work.

The spectrophotometric titration method is applicable on the microscale, and it has the advantage that the instrumentation is available in every laboratory. It is not, however, readily applicable to large numbers of samples with present instrumentation, though development of an efficient photometric Karl Fischer titrator seems to be feasible.

Electrometric Titration. By far the most commonly used instrumental method of Karl Fischer titration is the "dead-stop" amperometric technique with two platinum electrodes. A small potential (10-15 mV) is applied across these electrodes, and a galvanometer senses the current flow. To appreciate the chemistry taking place, consider a Karl Fischer back-titration, in which an excess of active Karl Fischer reagent is added to the sample and the unreacted reagent is back-titrated with standard water-in-methanol solution.

Before the end point both iodine and iodide are present, and at the applied potential electrolysis can take place, I_2 being reduced at one electrode and I^- being oxidized at the other, with a resultant flow of current. At (and after) the end point there is no I_2 present, so there is no reversible couple, no electrolysis can occur, and the current drops to zero.

In a direct Karl Fischer titration the current is zero before the end point, and it rises sharply after the end point.

Mitchell and Smith (2) have discussed titration assemblies, electronics, and applications of dead-stop Karl Fischer titration. Many commercial versions of the apparatus are available. In their simplest and least expensive form these consist of the electronic and titration vessel components, the titrant being delivered manually from a conventional buret. Highly sophisticated variations are also available in which the titrant addition rate and end point detection are microprocessor controlled, and the data are collected, analyzed, and stored by computer.

Potentiometric end point detection with two dissimilar metallic electrodes operating at a constant current of 10-100 μA has also been used for Karl Fischer titration. A commercial pH meter can be used as the potentiometer.

In coulometric Karl Fischer titration the iodine in the reagent is generated by electrolysis of iodide, and the extent of titration is measured in coulombs rather than in volume of titrant. The dead-stop amperometric method with two platinum electrodes is commonly employed as the method of end point detection.

Because of the accuracy with which iodine can be generated and measured coulometrically, the coulometric Karl Fischer titration method may be the best choice for extremely small amounts of water. The dead-stop amperometric method is a reliable, rapid, and very widely applicable technique for most Karl Fischer titrations.

APPLICATIONS

Concentrations of water ranging from parts per million to 100% can be determined by Karl Fischer titration, and amounts from micrograms to many milligrams can be determined. Most titrations are routine, but some samples may cause problems. A fairly common artifact that is observed is the occurrence of false end points or fading end points. If the sample is a nearly anhydrous nonpolar solvent it is not unusual to obtain a false end point, which may be due to the insolubility of the (polar) end products in the nonpolar medium; the solution to the problem is to incorporate some methanol or pyridine in the sample.

Another problem arises if the sample contains substances that can react, in the strongly dehydrating environment of Karl Fischer reagent, to yield water, resulting in a fading end point as water is generated. For example, a carboxylic acid can react with methanol to yield an ester plus water; this type of interference can be overcome by rapid titration or by using one of the modified reagents.

Yet another kind of problem occurs if the sample contains substances that can oxidize iodide to iodine, or that can react with iodine. For example, thiols are oxidized to disulfides by iodine. Somewhat elaborate countermeasures may have to be devised to circumvent such interferences (2).

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