Generalize Chemometric Protocol for Aquametry by Karl Fischer Titration

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ABSTRACT

Moisture content affects not only the physiochemical property of an organic or inorganic compound but also markedly deviate its stability if present beyond a specific concentration. Numerous methods were available and has been hand-to-hand adopted to determine the water content among which Karl Fischer titration hold a distinct position owing to its simplicity, accuracy, and cost effective measurement. The following paper presented here precisely defines some of the aspects of same.

Keyword: Karl Fischer titration, Aquametry, Karl Fischer reagent, alcohol

INTRODUCTION

Aquametry involves qualitative and/or quantitative measurement of water content in chemical compounds. Numerous techniques were available for determination of water content however Karl Fischer titration firmly holds the distinct platform in terms of specificity, sensitivity, & selectivity in chemometric aquametry, was pioneered by Karl Fischer (1935) and based on the philosophy of chemometric moisture content determination by a chemical reaction between water present in sample and Karl Fischer reagent. The technique now has been accepted as an official method for moisture content determination by most of the Pharmacopoeias (IP, USP, BP, NF) indicating its wide acceptability by global industrial as well as scientific community.

GENERALIZED PRINCIPLE

The Karl Fischer titration in its simplest form is a direct method of aquametry, estimating water content by calculating disappearance of iodine in a chemical reaction occurring itself between iodine and water molecule present in the sample. Initially during reaction, iodine gets reduced while sulphur dioxide is oxidized in the presence of water to yield HI and sulphur trioxide. The evolved sulphur trioxide reacts with pyridine to yield an inert salt complex termed as pyridine-sulphur trioxide complex, which further reacts with methanol yield pyridinium methylsulphate or pyridine salt of methylsulfate. The overall chemical reaction involved in Karl Fischer titration is summarizes as below;

$$I_2 + SO_2 + H_2O \rightleftharpoons 2HI + SO_3 \quad \ldots\ldots 1$$

$$SO_3 + C_5H_5N \rightleftharpoons C_5H_5NSO_3 \quad \ldots\ldots 2$$

$$C_4H_5NSO_3 + CH_3OH \rightleftharpoons C_5H_5NCH_3O\text{-}SO_3H \quad \ldots\ldots 3$$

The Karl Fischer reagent for the purpose of water content estimation can be prepared in the laboratory however it is recommended to use freshly prepared solution of same for better results. Commercially prepared reagents can alternatively also be employed with good success rate however they are costlier than former and must be standardized prior to use. As per U.S.P, the composition of Karl Fischer reagent includes iodine (125 g), pyridine (170 ml), methanol (670ml) & liquid sulphur dioxide (100ml).

Commonly it has been observed that Karl Fischer reagent prepared in excess methanol was unstable and required standardization prior to use. This problem can be effectively minimized by using methanol free reagent containing substituted alcohol rather than methanol. Likewise, the problem of sluggish end point, which is associated with anhydrous pyridine can be effectively overcome by using imidazole proving better sharp end point.

Preparation and Standardization of Karl Fischer Reagent

The general routine procedure for preparing Karl Fischer reagent includes initial mixing of anhydrous methanol (400ml) and anhydrous pyridine (80g) in a clean combustible flask. The flask is then immersed in an ice bath, slowly and steadily dried sulphur dioxide is bubbled into the flask containing methanol-pyridine mixture until it weight increased by 20g. Now iodine (45g) is transferred and shaken until it dissolves completely. The so prepared solution is placed in an air tight amber colored bottle for 24 hours and must be standardized prior to use.

The Karl Fischer reagent can be standardized by using any one of the procedure as given below;
Standardization with water-methanol system: Prepare 0.2% v/v water-methanol solution by adding 2.0ml of water to 1000ml of anhydrous methanol. From this, accurately measure 25ml of solution, and titrate it with Karl Fischer reagent. The net content of water mg/ml of water-methanol system can be calculated mathematically by formula as given below;

W=V.E/25

Where,
W= water content mg/ml
V=Volume of Karl Fischer reagent required
E=Water equivalence factor determined against sodium tartrate

Standardization by sodium tartrate: Measure 30ml of anhydrous methanol, transfer it into a clean suitably dried reaction vessel, slowly transfer (dropwise) Karl Fischer reagent untill to get an end point. Once end point is reached, immediately add 150-350mg of sodium tartrate dehydrate and titrate again to end point. The water equivalence factor E (mg/ml) of reagent can be calculated by formula given below;

E = 0.1566.w/v

Where,
E =Water equivalence factor
w=Weight of sodium tartarate (mg)
v=Volume of reagent required (ml)

Precautions During Titration

1. The freshly prepared reagent must be standardized prior to an analytical work-up.
2. All glass wares and apparatus used for preparing/standardizing the reagent must be free from water.
3. The freshly prepared/commercially available reagent must be placed in a tightly closed container.
4. Every necessary care must be taken to avoid exposure of reagent with moisture.
5. The sample used for aquametry must be free from following compounds as they interfere with end point:
    a. Oxidizing agents
    b. Reducing agents
    c. Basic oxides and their salts
    d. Aldehydes and ketones

Methods of Karl Fischer Titration

Volumetric and/or columetric are two well established methods principally used for estimation of water content by Karl Fischer titration. The former method is used for sample containing high amount of water and is based on simple principle of total amount of water present in sample is equal to net amount of Karl Fischer reagent used during titration. On other hand later is advantageous for sample containing low quantity of water with an aid of coulometer.

CONCLUSION

Karl Fischer titration is an unquestionable technique for aquametry of sample containing high as well as low content of water. The wide acceptance of technique by scientific as well as industrial community indicates its validity and authenticity however sample size, standardization of reagent, and total deprivation of moisture content are some of its limitations.

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