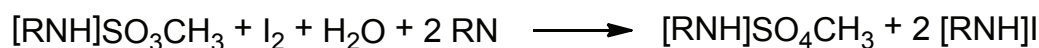
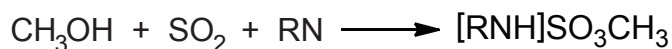


THE BASICS OF KARL FISCHER TITRATION

Karl Fischer titration is an analytical technique to measure the amount of water contained in various samples, which may be solid, liquid or gaseous. This method was originally developed in the 1930s by German chemist Karl Fischer.

Karl Fischer titration is based on a 1:1 reaction between iodine and water in the presence of sulfur dioxide and a base. Below is the 2-step mechanism of the reaction:



From the reaction mechanism, it's evident that the reagent used for the titration needs to contain the following:

- Alcohol - methanol was used originally, but in different variations of the reagent can be replaced by ethyl carbitol, methoxypropanol, ethanol, etc.
- Sulfur dioxide
- Iodine
- Base - pyridine was used initially, but has since been replaced by imidazole, which assures a higher rate of reaction and is less toxic

One of the most important developments in Karl Fischer titration chemistry was the replacement of pyridine with imidazole. Pyridine is a relatively weak base and the equilibrium of the reaction is not completely shifted toward the products. As a result, use of pyridine-based reagents typically resulted in slow reactions and unstable endpoints. This, in turn, negatively impacted reproducibility of measurements.

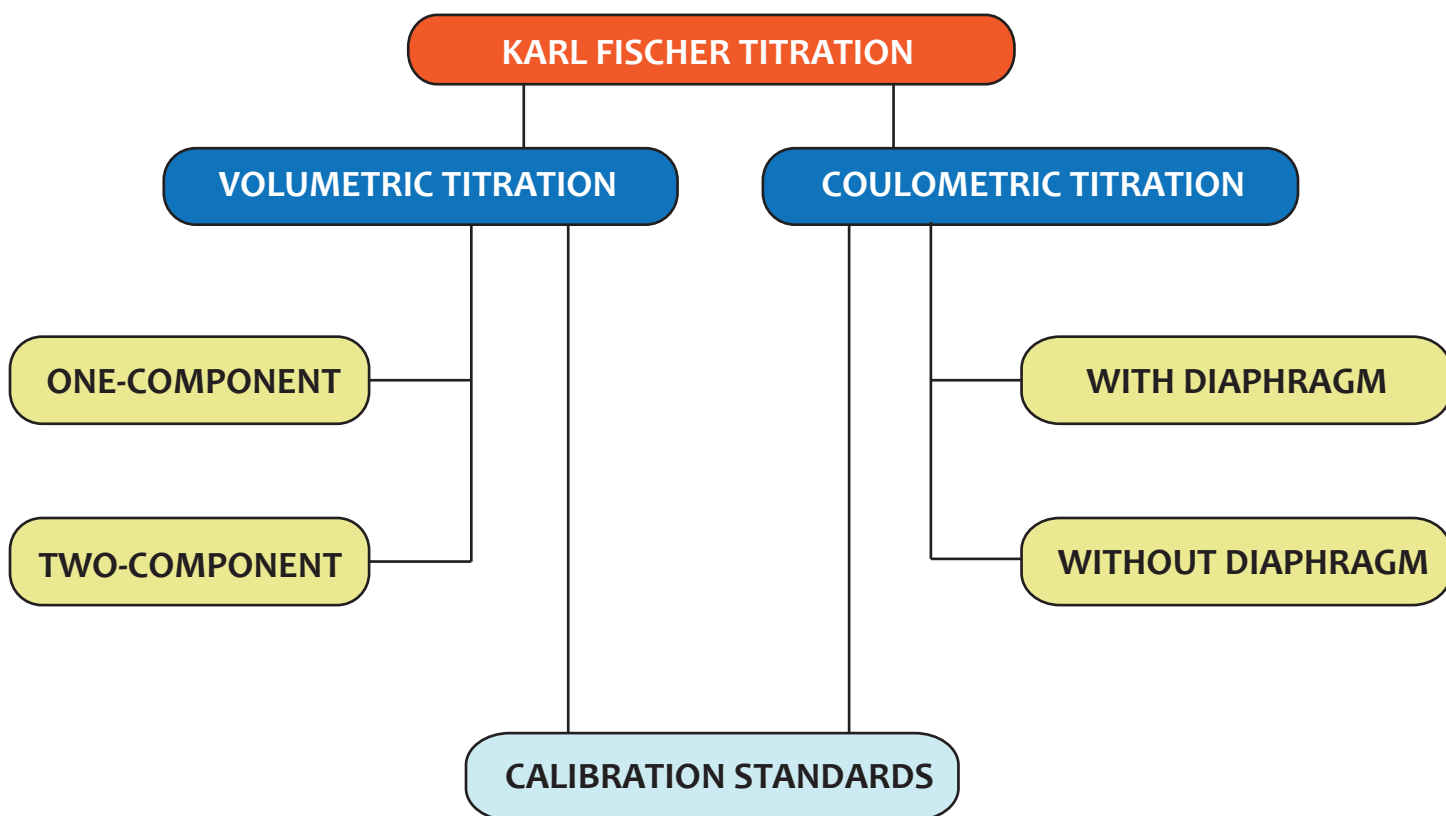
Imidazole is a stronger base and shifts the reaction equilibrium completely to the right, which results in a faster titration rate and more stable endpoints.

TYPES OF KARL FISCHER TITRATION

Karl Fischer titration is based on the stoichiometric reaction of iodine with water. There are two methods of introducing iodine into the sample - addition of molecular iodine in a solution with a volume of a reagent (volumetric titration) and generation of iodine electrochemically within the titration cell (coulometric titration).

Volumetric titration has the benefit of speed and generally lower cost, while coulometric titration allows for accurate analysis of samples with low moisture levels.

The two main methods have their own variations and both make use of calibration standards to determine titer of volumetric reagents and verify accuracy of measurements.



VOLUMETRIC KARL FISCHER TITRATION

Volumetric determination of water can be done with one-component or two-component titration.

In one-component titration, all of the reactants needed for the reaction are present in a single solution. Two-component titration uses two solutions - one of them is a solvent that contains sulfur dioxide and the base and the other is the titrant, which is a solution of iodine in methanol or another suitable solvent.

In both cases, the sample is dissolved in the solvent/ working medium and is contained in the titration cell.

The iodine-containing titrant is added, typically by a dosing pump. The water content in the sample is then calculated based on the volume of the reagent.

Commercial titrators normally automate the process and integrate all components of the instrument.



WaveTrace™ line of reagents covers both one- and two-component titration methods.

	Composit T5/T2/T1	Composit K5/K2	Titrant T5/T2	Titrant K5/K2	Methanol Sharp	Solvent	Solvent KT	Solvent C	Solvent CX	Solvent D	Solvent F
General one-component titration	●				●						
General two-component titration			●			●					
Aldehydes & ketones		●		●			●				
Crude oil & petrochemicals	●							●	●		
Biofuels	●							●		●	
Oils, fats and long-chain hydrocarbons	●									●	
Carbohydrates	●										●

VOLUMETRIC KF TITRATION

One-component titration is the most common, due to its simplicity and convenience.

Two-component titration may still be selected for its high rate of reaction, which produces very sharp endpoints and highly reproducible results. In addition, Titrant T5 and T2 have a virtually unlimited shelf life.

The titrants for two-component analysis must be used with WaveTrace™ Solvent to produce the complete reaction medium.

Methanol is not the only solvent that can be used as working medium for one-component titration, however the choices are limited. The solvent needs to be sufficiently polar and protic, thus restricting selection to compounds with hydroxyl groups and high overall polarity. In addition, they need to dissolve a variety of samples, which further limits available options. As an example, methoxypropanol can be used as a solvent and it is the basis for Solvent KT. However, the reaction rate is lower than in methanol and the endpoint is not as well defined.

These considerations need to be taken into account when attempting to modify the standard solvents to work with difficult to dissolve samples. For instance, chloroform, long-chain alcohols or aromatic solvents may be added. But the fraction of methanol should never be lower than 40% by volume. If the concentration of methanol or similar solvent is too low, reaction stoichiometry may change and produce incorrect results.

Composit T5/T2/T1 reagents can be used with dry methanol, but WaveTrace™ Methanol Sharp is the preferred working medium. It has been formulated to accelerate the reaction rate and produce exceptionally sharp titration endpoints.

VOLUMETRIC KF REAGENTS: TITER AND REAGENT CALIBRATION

Determination of water content using volumetric Karl Fischer titration is based on the stoichiometric reaction between the components of the reagent and moisture contained in the sample. Capacity of the reagent to react with water is expressed in terms of a titer, or water equivalent (WE).

Titer indicates the amount of water that can be consumed by 1 ml of a given reagent.

$$\text{Titer (WE)} = \text{Weight of water (mg)} / \text{Volume of reagent (ml)}$$

For example, if a Composit T2 reagent has a titer of 2.1 it indicates that 1 ml of this reagent will neutralize 2.1 mg of water present in a sample. When the titer is known, water content in the sample can be easily calculated from the quantity of reagent used to achieve the endpoint.

WaveTrace™ Karl Fischer reagents are manufactured with several standard titers. Composit series may have titers of 1, 2 and 5, which are indicated by the name of the specific reagent (T1, T2 and T5, respectively). The general rule is that the greater the anticipated water content in the samples, the higher titer reagent should be used. While theoretically Composit T5 could be used for any water determination, in practice it may be too coarse for accurate analysis of samples with low moisture content.

The titration vessel must be kept as airtight as possible to avoid reagent reacting with ambient moisture contained in the air, which reduces the titer and may cause fading of the endpoint (especially for low titer reagents). It is also recommended that the titration system is flushed with fresh reagent before the analysis, in order to eliminate the accumulated moisture in the tubes and other components of the system.

Titer stability and reagent calibration

WaveTrace™ reagents are formulated for maximum stability and maintain their titer within specification for long periods of time. However, once the bottle is opened and the reagent is being used, ambient moisture diffuses into the bulk of the solution and consumes some of the reagent. This process reduces the effective titer and requires a recalibration before use, in order to assure accurate results.

There are two main methods of calibration, both based on providing a standard sample with a known water content. The first method uses a water sample dissolved in an organic solvent at a known concentration. The second method makes use of sodium tartrate dihydrate crystals that contain 15.66% of water by weight.

TITER DETERMINATION WITH STANDARDS

Calibration of WaveTrace™ reagents using sodium tartrate dihydrate

Sodium tartrate dihydrate (STD) forms a stable complex with water at a known saturation concentration (15.66%) and retains this level even at temperatures over 120 °C. Since STD exists as crystals, it is easier to handle and can be weighed with high accuracy using standard analytical balances. The quantity of STD normally depends on the anticipated titer of the reagent, with greater amounts used for higher titers. For example, we recommend using 150 – 200 mg of STD to calibrate Composit T5 reagent. Similarly, 75 – 100 mg of sodium tartrate dihydrate would be more appropriate for calibration of Composit T2.

Once the crystals are weighed, they are added to the titration vessel. Care must be taken to ensure that the crystals are fully dissolved before beginning the addition of the reagent. At this point, the reagent is added as in a regular titration until the endpoint is reached. The titer (water equivalent) is calculated as follows:

$$\text{Titer (WE)} = \text{Weight of STD (mg)} * 0.1566 / \text{Volume of KF reagent (ml)}$$

Calibration of WaveTrace reagents using liquid water standards

Liquid water standards offer the same features as the sodium tartrate dihydrate. The STD crystals can be weighed easily and do not require any special handling. However, sodium tartrate dihydrate may not fully dissolve in some reagents, such as WaveTrace™ Solvent KT and some third-party ethanol-based reagents. To avoid this issue, liquid water standards represent a more reliable alternative.

Liquid water standards are typically available in sealed glass ampoules and have a known water content, typically 10 mg per 1 g of the standard. The exact value is specified on the Certificate of Analysis supplied with the standard.

The standard solution is added to the titration vessel using a syringe in exactly weighed 1 g portions. Then the reagent is added and titration is carried out to the endpoint. The titer (water equivalent) is calculated as follows:

$$\text{Titer (WE)} = \text{Weight of sample (g)} * \text{Water content in CoA (mg/g)} / \text{Volume of KF reagent (ml)}$$

The choice between the two types of standards should be made based on the reagents being calibrated (solubility) and by experimentally comparing results from both methods. Ideally, titer should be verified by titrating a standard water solution (such as SRM 2890 available from NIST) to make sure it has been determined correctly.

VOLUMETRIC KF TITRATION WITH COMPOSIT T5/T2/T1

Composition

WaveTrace™ Composit is a line of one-component Karl Fischer reagents for volumetric determination of moisture. The reagents include Composit T5, Composit T2 and Composit T1, which differ by titer.

Any WaveTrace™ Composit reagent contains all components required for a stoichiometric reaction of iodine with water in the sample. The components include sulfur dioxide, imidazole and iodine dissolved in diethylene glycol monoethyl ether.

WaveTrace™ Composit reagents are formulated to retain their titer within specification for at least 5 years. The typical loss of titer is less than 3% per year.

Recommended Solvents

WaveTrace™ Composit reagents can be used with any methanol-based solvent for a stoichiometric reaction with reproducible results. For best results, WaveTrace™ Methanol Sharp should be used, since it produces an exceptionally stable and easily detectable titration end point. In some cases, a specialized solvent is required. For titration of aldehydes and ketones, use WaveTrace™ Solvent KT. For titration of petrochemicals, biofuels and other samples poorly soluble in methanol, use WaveTrace™ Solvent CX, Solvent C, Solvent D or Solvent F. For specific selection criteria please refer to the table at the beginning of the volumetric titration section.

Testing Procedure

The titration cell must be dry and free of residue from previous measurements.

1. Add WaveTrace™ Methanol Sharp or another suitable solvent to the titration cell. The exact volume varies with the model of the instrument and ranges from 30 to 100 ml.
2. Fill the burette or connect the bottle with WaveTrace Composit reagent to the dosing pump.
3. Add WaveTrace™ Composit reagent until the end point is reached and the solution in the titration cell contains no water.
4. Determine the exact titer of the reagent using a water or STD standard. Reach the endpoint.
5. Add a sample of known weight.
6. Titrate the water content with WaveTrace™ Composit T5/T2/T1 (depending on the anticipated water content and application).

VOLUMETRIC TITRATION OF ALDEHYDES AND KETONES

WaveTrace™ K Series reagent line is formulated for analysis of samples containing aldehydes and ketones. The distinctive characteristic of the K Series is the absence of methanol, which is commonly used in other Karl Fischer reagents. The composition of the reagents is formulated to prevent side reactions that occur in solutions of compounds with carbonyl groups that can undergo a nucleophilic reaction with alcohols with the formation of acetals (Figure 1). One of the products of this reaction is water, which interferes with the results of analysis and causes instability of titration endpoints.

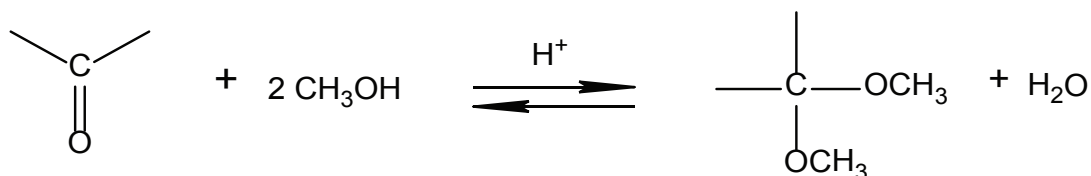


Figure 1. Formation of ketals in the reaction of acetone with methanol

WaveTrace™ K Series reagents are also designed to prevent bisulphite addition to aldehydes (Figure 2). This second side reaction consumes a portion of the water content in the neat specimen and results in erroneously low water content measurements.

WaveTrace™ Composite K5 is a variant of WaveTrace™ Composite T5, with a formulation for a slightly slower reaction rate to minimize interference from the bisulphite addition side reaction.

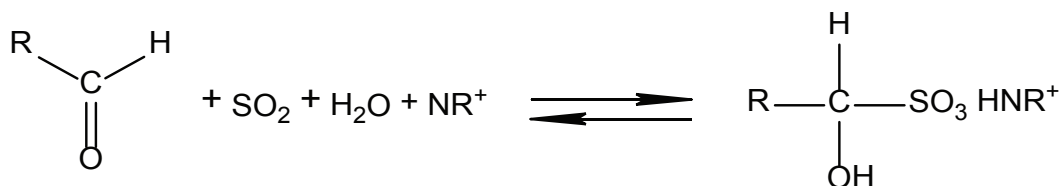


Figure 2. Bisulphite addition to aldehydes that consumes water. NR+ is a base.

WaveTrace™ K Series of reagents for aldehydes and ketones includes solution systems for both one-component and two-component KF titration:

- One-component system includes Composite K5 and Composite K2 reagents, as well as Solvent KT. They are methanol-free and include components that inhibit side reactions.
- Two-component system includes Titrant K5 and Titrant K2, with Solvent KT suitable for use with these reagents. This titration method allows for a more accurate moisture determination with slower side reactions and a more stable titration end point.

TITRATION OF OILS, BIOFUELS AND OTHER SPECIAL SAMPLES

Methanol is the solvent of choice in the majority of situations. However, many samples have low solubility in methanol, thus requiring a different solvent for volumetric titration. In order to handle these situation, Quveon has developed a number of solvents that are ready for use out of the box.

The naming convention adopted by Quveon helps easily identify the solvent required for a particular application and is based on the first letter of the primary solvent(s) added to the formulation.

WaveTrace™ Solvent C contains chloroform and should be used for titration of fuels and general organic compounds with low methanol solubility.

WaveTrace™ Solvent C contains chloroform and xylene and is the best choice for crude oil, heavy hydrocarbons, transformer oils and other similar samples.

WaveTrace™ Solvent D contains 1-decanol and is best suited for titration of oils, fats and long-chain hydrocarbons. The most common applications are analysis of biofuels, plant oils and fatty acids.

WaveTrace™ Solvent F contains formamide and is formulated for analysis of carbohydrates, including glucose, starch, dextrin and other sugars.

IMPORTANCE OF pH

Karl Fischer reaction has an optimum pH range between 5 and 7.5. If pH is below 2, the reaction does not occur at all. In very basic conditions, iodine is consumed in side reactions and leads to false high values.

Since increased acidity leads to a drop in the reaction rate, acidic samples need to be neutralized. Weak bases, such as imidazole, can be used to bring pH into a more neutral range.

In case of basic samples, weak organic acids are recommended. Benzoic or salicylic acids are good choices. The exact amount will vary depending on the pH of the initial solution, but can be between 5 and 15 g per 60 ml of solvent.

COULOMETRIC KARL FISCHER TITRATION

In coulometric KF titration, iodine is generated electrochemically and its amount is proportional to the amount of electricity passed through the solution. Once the titration endpoint is achieved, the current is turned off and the final amount of electricity is used to calculate how much iodine was required for the titration.

Coulometric titration can be carried out in two types of titration cells - with or without a diaphragm. Cells with a diaphragm were developed first and used a semi-permeable glass diaphragm to separate the volume of the cell into two chambers containing the cathode and the anode, respectively. The separation was used to isolate the individual electrode processes and avoid reduction of iodine back to iodide.



Cells without a diaphragm were developed in late 1980s. They allow for a simpler setup and only require one reagent solution. In addition, a diaphragm introduces additional electrical resistance, which can lead to overheating of the solution and limit the maximum current. The specific material of the diaphragm can also impact the drift in the anode and cathode chambers, thus adding a source of error.

Currently, cells without a diaphragm are more common. However, cells with a diaphragm have the advantage of separation from the anode chamber where the samples are added. When multiple samples have been added, the composition of the anolyte changes and can impact reproducibility of consecutive measurements. In cells without a diaphragm, the anolyte reagent has to be changed more frequently to avoid this issue. Cells with a diaphragm help alleviate this problem for samples with very low moisture content that need to be added in large amounts.

REAGENTS FOR COULOMETRIC TITRATION

The basic reagent used in most of the coulometric titrations is WaveTrace™ Coulometric AGR, which is the general purpose analyte solution for titration with or without a diaphragm. Different types of samples require different variants of the reagent, mainly to address solubility issues.

In cells with a diaphragm, WaveTrace™ Coulometric CGR is required and can be used with any of the specialized coulometric reagents, as listed in the table below.

	Coulometric AGR	Coulometric AGR-C	Coulometric AGR-Oil	Coulometric AGR-Oven	Coulometric AHR	Coulometric CGR	Coulometric AGR-AF7	Coulometric CGR-AF7
General titration with a diaphragm	●					●		
General titration without a diaphragm	●							
Titration of biofuels and oils		●	●			●		
Titration of crude oil and petrochemicals			●			●		
Titration with oven				●				
Titration of oils, fats and long-chain hydrocarbons		●			●			
Titration with Orion AF7							●	●

The Coulometric CGR reagent has an increased viscosity compared to most existing reagents, which leads to a much lower interference with the analyte content across the diaphragm. This feature translates into higher accuracy with a lower relative error of measurement. WaveTrace™ Coulometric CGR is formulated to be non-hygroscopic and allows packaging in 110 ml bottles instead of the traditional single-use ampoules.

COULOMETRIC TITRATION OF PETROCHEMICALS AND BIOFUELS

Samples containing oils, biofuels and petrochemicals usually have limited solubility in methanol. Specialized reagents have been formulated to dissolve these samples and retain stoichiometry of the reaction. For example, Coulometric AGR-C is an anolyte solution with added chloroform, which is suitable for most oils and biofuels. It can be used with Coulometric CGR in cells with a diaphragm.

In cases of crude oil or petroleum products, it is recommended to use Coulometric AGR-Oil, which contains chloroform and xylene.

It should be noted that addition of non-polar solvents also increases electrical resistance of the solution. Higher electrical resistance may lead to overheating of the solution when titrations take a long time. Therefore, it's important to pay attention to the temperature of the cell and periodically allow it to cool in order to avoid excessive evaporation of the solution.

Samples containing crude oil, petrochemicals and biofuels most frequently are titrated in cells with a diaphragm. It prevents the samples from contaminating the cathode and maintains constant composition of the cathode solution. In cells without a diaphragm, these samples can dramatically alter electrochemistry of the cell and negatively impact accuracy. This is especially true for low moisture samples that have to be added in large amounts (up to 10 ml). After only several measurements, the solution becomes so diluted by non-polar components that the current efficiency at the cathode can substantially decrease and lower its performance.

Samples containing long-chain hydrocarbons can in some cases be dissolved in AGR-C and AGR-Oil reagents. However, the best choice in this situation is Coulometric AHR, which is based on decanol as the solubilizing agent. It ensures correct stoichiometry and optimal solubility of the sample along with high current efficiency.

COULOMETRIC TITRATION WITH OVEN

In some cases, samples contain components that do not dissolve in any of the available reagents or cause side reactions that are difficult to prevent. In this situations, titration with oven can provide a good alternative.

A drying oven can also be used for samples that only release water at elevated temperatures, such as plastics and resins.

The oven is used to elevate the temperature of the sample and evaporate the moisture, which is then delivered to the titration cell with a carrier gas. Since the moisture is delivered in gas phase and at an elevated temperature, the reagent must be able to dissolve it without boiling.



WaveTrace™ Coulometric AGR-Oven has been designed specifically for this purpose and contains propylene glycol to control the boiling point of the reagent.

TECHNICAL SUPPORT BY QUVEON

If you have technical questions about use of WaveTrace reagents or selection of the appropriate reagent for your application, please contact our Technical Support team:

Phone: 1-800-471-3575
Email: support@quveon.com
Web: www.quveon.com

We can help you with any of the following:

- advice on reagent/titrator application
- custom reagents
- method development
- technical literature
- Safety Data Sheets
- regulatory questions