

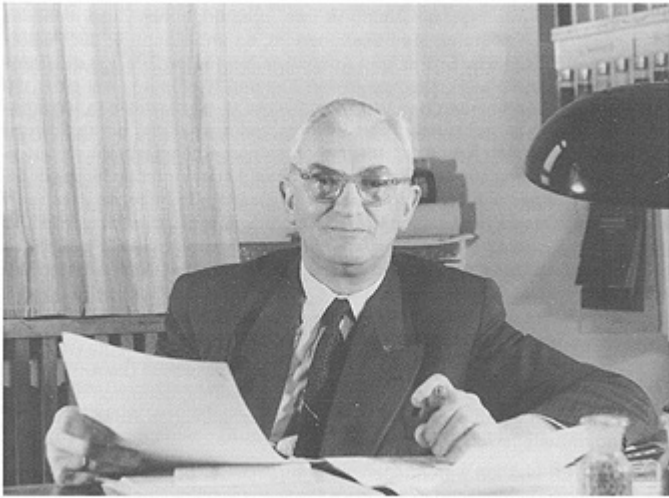
ThermoFisher
S C I E N T I F I C

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Summary of Karl Fischer Titrations

Orion Products,
Beverly, MA

Who is Karl Fischer?



Karl Fischer 1955

- Karl Fischer was the scientist who in 1935 developed the original Karl Fischer method for water determination using pyridine, sulfur dioxide, and iodine.
- Since that time, the reagents have been improved to make the titrations faster with better endpoints, but the process still uses an organic base compound, sulfur dioxide, and iodine as the basis of the reaction (with the addition of an alcohol, usually methanol or ethanol).

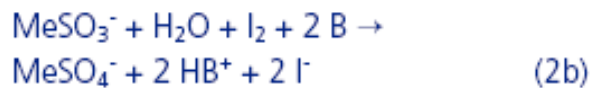
What is a Karl Fischer Titration?

- A Karl Fischer titration determines the water content in a sample, based on an iodine/iodide redox reaction.
- It is a titration method where water reacts with iodine until the water is consumed and the endpoint is reached.

1. step



2. step



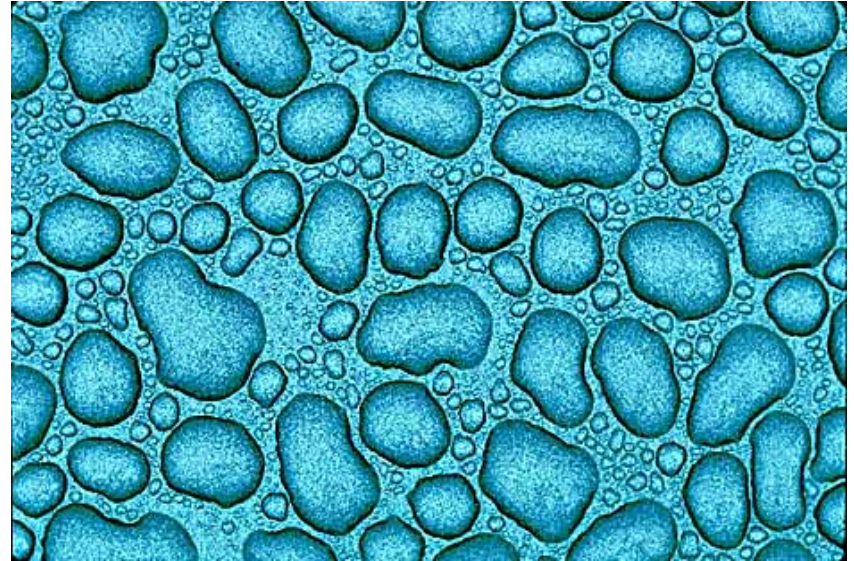
B = Base

- A Karl Fischer moisture determination is advantageous, as compared to a determination based on weight loss, because KF is not affected by volatile compounds.

Who Measures Moisture and Why?

Customers:

- Quality Control Labs
- Process Labs
- General Chemistry
- R&D Labs
- Analytical Labs
- Manufacturing



Water:

- *Changes The Properties Of Products*
- *Causes Corrosion*
- *Reduces The Storage Quality Of Food, Medicine, And Cosmetics*
- *Reduces The Yield Of Chemical Reactions*
- *Affects The Flowability Of Products*

Where is the Karl Fischer Titration Used?

- Matrices include: liquids, solids, gases, pastes, oils

- Markets include:
 - Food
 - Pharma
 - Petroleum products
 - Chemicals
 - Environmental – wastes and soils
 - Consumer Products
 - Paints
 - Plastics

Volumetric and Coulometric Titrations

- Iodine is either added directly to the titration cell in a reagent (volumetric titration) or generated by passing current through an electrolytic cell containing iodide (coulometric titration).
- Volumetric titration – water determination based on volumetric measurement of reagent. Good for high level moisture determinations.
- Coulometric titration – water determination based on measurement of time and current (in coulombs) used to generate the iodine. Good for low level moisture determinations.

Volumetric Versus Coulometric Karl Fischer

■ Volumetric

- Dispenses Titrant
- Calibrate w/Standards
- Solids or Liquids
- 50 ppm Limit
- Most Common
- Water = # Motor Steps Compared to Standard
- Endpoint is Detected via Platinum Electrode

■ Coulometric

- Uses Current
- Generates Iodine between Cathode and Anode Electrodes
- No Calibration
- Liquids only
- Lower Detection Limit than Volumetric at 1 ppm
- No Peristaltic Pump

Orion Karl Fischer Offerings - Instruments

	AF8	Turbo2	AF7/AF7LC
Instrument Type	Volumetric	Volumetric	Coulometric
Best for	Liquids	Solids	Low moisture samples
Water Content	10 ppm to 100% water	50 ppm to 100% water	1 ppm to 100% water (10 ug min)
Matrices	Liquid, solid, gas	Liquid, solid, gas	Liquid
Advantages	All around performance, pricing	Best for solid, pastes, oils that require sample prep; avail water jacket for temp control	Low detection limit, pricing (AF7LC)

Orion Karl Fischer Applications



Orion Turbo2®

- >50 ppm – 100% Moisture
- Ideal for Pharmaceutical and Food Samples
- Potato Chips
- Cellulose
- Sugar Cane
- Licorice or Gum
- Chocolate and other Confections
- Tablets such as Vitamins or other pills



Orion AF8

- <50 ppm – 100% Moisture
- Liquids and Powders
- Motor Oils
- Surfactants
- Citric Acid
- Polyols or Urethanes
- Surface Sugar
- Aspirin
- Cooking Oil



Orion AF7

- 1 ppm – 100% Moisture
- Coulometric Titrator for Low-Level and High-Level
- Resins
- Insulating Oil
- Gasoline
- Diesel Fuel
- Transformer Oil
- Solvents



Orion AF7LC

- 1 ppm – 5% Moisture
- Solvents
- Insulating Oil
- Gasoline
- Diesel Fuel
- Transformer Oil

Karl Fischer Offerings - Accessories

- Water-jacketed titration vessel (Turbo2) for temperature control
 - lower temperature to control side reactions
 - Higher temperature to speed dissolution
- Marprene pump tubing (Turbo2 and AF8) for use with two-component reagent systems
- Balance interface – cables to interface with various makes of balances
- Printer interface – cables to interface with external printers

Volumetric vs. Coulometric Titration Reagents

Titration Type	Volumetric		Coulometric
	One-Component	Two-Component	Anolyte/Catholyte
Reagents	Reagent (titrant)	Titrant	Generated coulometrically from iodide in the anolyte
Source of iodine	Reagent (titrant)	Titrant	Generated coulometrically from iodide in the anolyte
Source of SO ₂ , alcohol, and base	Reagent (titrant)	Solvent	Anolyte
Advantages	Unlimited water capacity, different titres available, widely used	Faster titrations than one-component, better accuracy for low water contents, higher buffer capacity, stable titre	Suitable for lowest water contents, highly accurate
Disadvantages	Can be slower than two-component titrations	Costs more	Slow for high water content, proper operation requires more care

Special Reagents Available

- Special Reagents include:
 - Formulations for determination of water in aldehydes and ketones
 - Buffers for acidic samples
 - Buffers for basic samples
 - Acids to neutralize basic samples
 - Base to neutralize acid samples
 - Pyridine as the base (older/traditional formulation)
 - Solvent mixes for better dissolution of difficult matrices, such as fats, oils, proteins, etc.
 - “non-toxic”, methanol-free
 - Chloroform/hydrocarbon-free

Sources of Reagent Chemicals

- Sources include:
 - Thermo Fisher Scientific – Aqualine® Karl Fischer Reagents
 - Riedel-de Haen (Sigma-Aldrich) Hydranal®

Standards for Karl Fischer Titrations

	Pure Water	Standard Solutions	Solid Standards
Used for	Standardization	Standardization, verification	Standardization, verification
Water Content	1000 mg/ml	1, 5, or 10 mg/ml	15.66% (15.66 mg water per 100 mg sodium tartrate -2-hydrate)
Advantages	Readily available, inexpensive, high water content testing	Good for low water content testing	Good for solids testing, often preferred for USP testing

Factors to Consider in KF Titration

- pH: pH 5-7 is ideal. Use acid, base, or buffer if necessary.
- Aldehydes and ketones: use special reagents to prevent side reactions which generate or consume water and prevent good endpoints
- Water content: consider when choosing AF7, AF8, or Turbo 2.
- Sample size: choose sample size that is large enough for precise determination but not so large as to prolong the titration, exceed the capacity of the reagent, or be insoluble. For volumetric, aim for 25 mg of water. For coulometric aim for 0.1 to 5 mg water.
- Frequency of Solvent/Working Medium Change: when the vessel is full, when the methanol content is <25%, when the capacity of the solvent is exceeded (generally not more than 1 mg water per 1 mL methanol).

Factors to Consider in KF Titration (cont.)

- Exclusion of background water: maintain desiccant tubes, keep reagents dry, good seals on instrument and reagent bottles
- Pretitration/conditioning of working solution: solvent/working solution must be dry but not overtitrated before the sample titration to avoid positive or negative bias to results.
- Dissolution of the sample: sample must be completely dissolved prior to the start of the titration to obtain accurate and reproducible results. Choose the right solvent, allow sufficient time for dissolution (extract time), increase temperature, grind sample.
- Conductivity: Conductivity of the solvent and added sample has to be sufficient to support proper function of the electrodes in order to detect the endpoint and/or generate the iodine titrant (coulometric).

Resources Available

- www.thermo.com/water: follow link for Applications and Technical Resources, then View Applications by Parameter, to Titrations - Karl Fischer Moisture, and select for listings.
- Instruction manuals: each Orion manual has a section at the back titled “Fault Finding Guide” or “Trouble Shooting Guide” which suggests solutions to common problems.
- Fisher Scientific Aqualine® Reagents, customer service 1-800-766-7000.
- Orion technical service at 1-800-225-1480 or contact your local sales representative.