Karl Fischer Analysis of Fuel Ethanol

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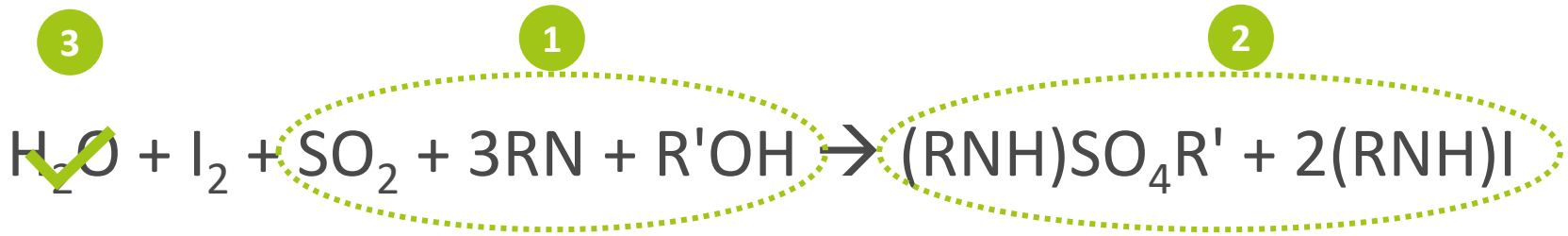
Today’s Session

- Review KF reaction
- Volumetric vs. coulometric
- Choosing the right sample size
- Common hurdles
- Q&A
- Additional Resources

Karl Fischer Reaction

1. Alkylsulfite reactive intermediate
2. Sulfite group oxidized to sulfate group by iodine
3. One mole of water is consumed

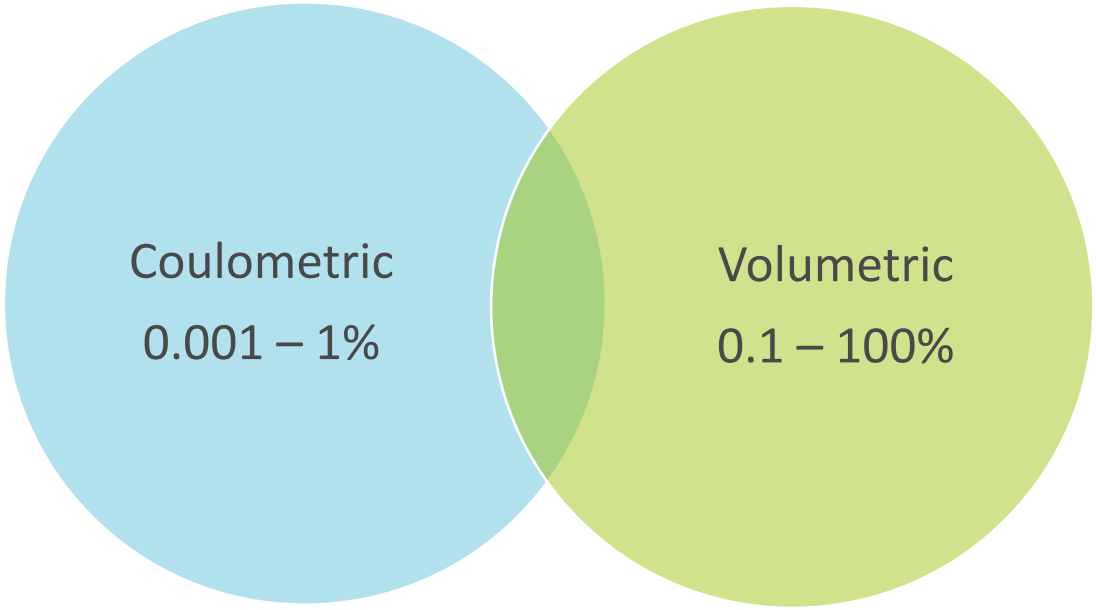


By knowing volume of iodine consumed, water concentration is directly determined

Karl Fischer Techniques

Choose a technique based on:

- Expected moisture concentration
- Available sample
- Sample solubility



ASTM D7923 Procedure A

ASTM D7923 Procedure B

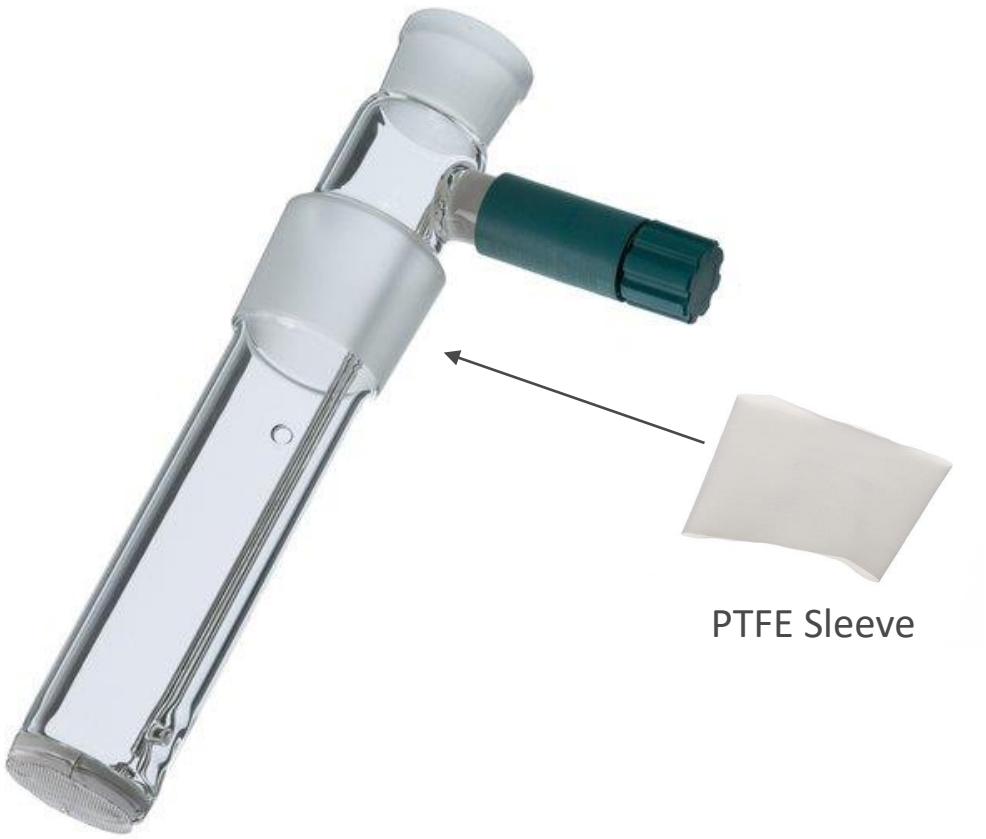
Coulometric Karl Fischer

- 0.001% - 1% range
- Iodine generated from iodide containing reagent using current
- Generating current switched off with detection of slight excess of free iodine
- Amount of iodine generated is known from charge and time

Double Platinum Electrode

- Indicates excess iodine in volumetric and coulometric systems
- Coulometric systems – use PTFE sleeve; not grease
- Pins should be parallel
- Clean as needed and store dry (or in vessel)
- Damaged electrode or cable can appear as overtitration

Generator Electrode



- Generates iodine from iodide solutions by applying current
- Handle delicately, do not bend mesh or connections
- Dirty electrode:
  - Sluggish response
  - Decreased iodine generation
  - Mesh/diaphragm turns gray
- Cleaning procedure:
  - Rinse with water or solvent
  - 50% nitric acid soak (10-15 minutes)
  - Rinse with water, then methanol, then dry

Volumetric Karl Fischer

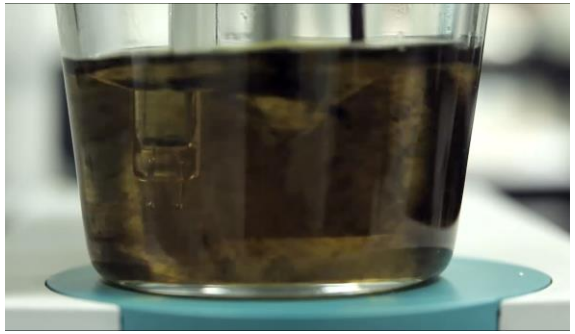
- 0.1 – 100% range
- Solvent solution consists of methanol
- Titrate with iodine reagent
- Fast titrations
- Solids, liquids, gases
- Very modifiable system
  - Solubility promoters
  - Homogenizer
  - Temperature

Cleaning Karl Fischer Titration Vessels

Coulometric vessels are single piece with glass joints

Volumetric vessels have separate parts and often use o-rings

1. Empty vessel and rinse with solvent
2. Wash with soap and water
3. Rinse with solvent
4. Soak in 50% nitric acid for 10-15 minutes
5. Rinse with water
6. Rinse with solvent
7. Dry in oven < 60°C



ASTM D7923
Procedure A - Coulometric

- Water up to 2% by mass
- Pre-titrate or condition KF vessel
- Rinse syringe with sample
- Withdraw appropriate sample amount
- Invert the syringe to eject air
- Wipe excess needle from syringe
- Obtain mass of syringe containing sample to ±0.1 mg
- Inject sample below the level of the KF solution
- Withdraw and weigh syringe to ±0.1 mg

TABLE 1 Recommended Sample Size (Coulometric)

Expected Water Content (mass percent)	Sample Size (g)
0 to 0.2	3 to 5
0.2 to 0.5	1 to 2
0.5 to 1.0	0.5 to1.0
1.0 to 2.0	0.5
>2.0	Please use Procedure B

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Procedure B - Volumetric

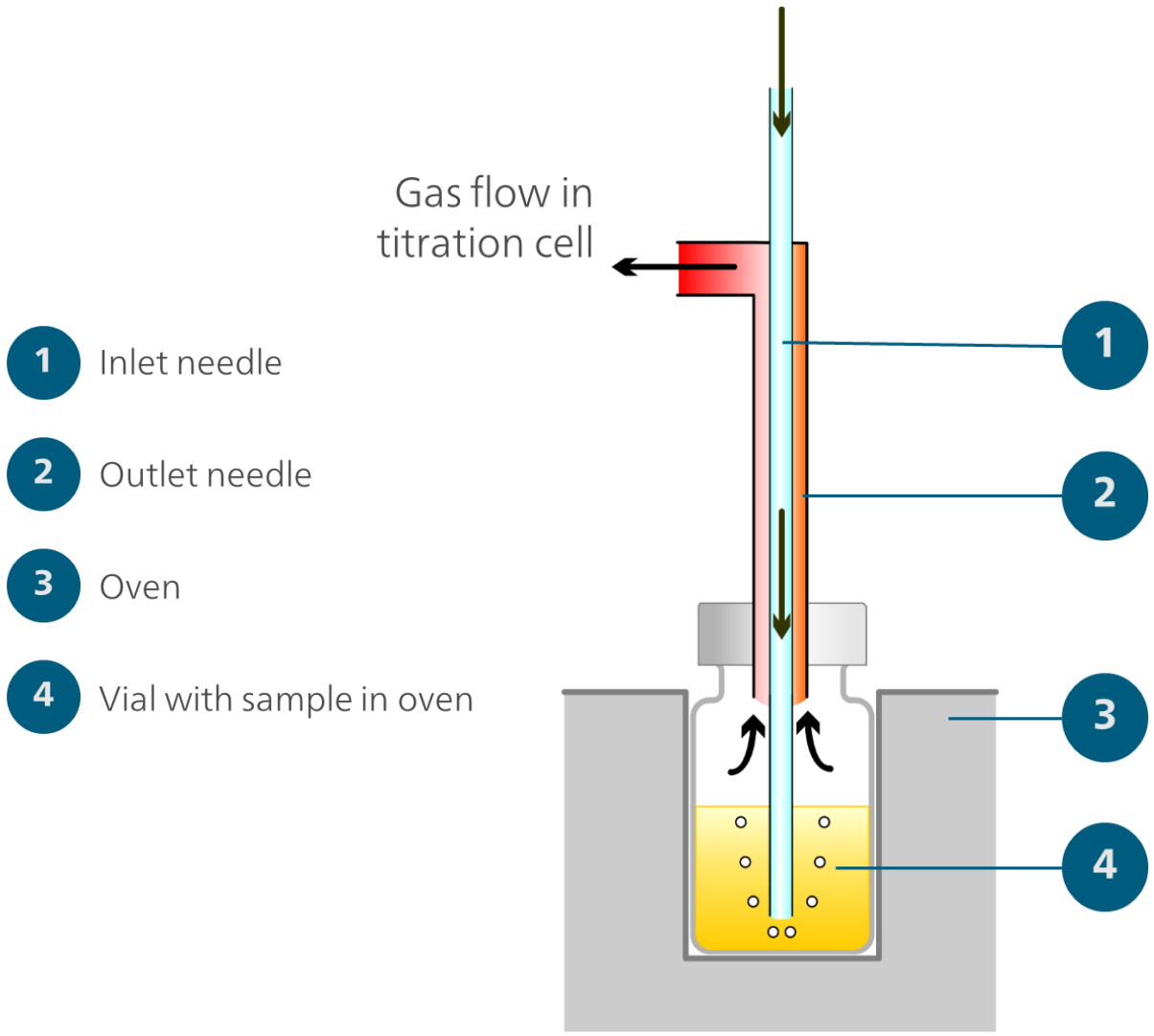
- Water up to 5.4% by mass
- Prepare buret and tubing
- Pre-titrate or condition KF vessel
- Rinse glass gas-tight syringe with sample
- Withdraw appropriate sample amount
- Invert the syringe to eject air
- Wipe excess needle from syringe
- Obtain mass of syringe containing sample to ±0.1 mg
- Inject sample below the level of the KF solution
- Withdraw and weigh syringe to ±0.1 mg

TABLE 3 Recommended Sample Size (Coulometric)

Expected Water Content (mass percent)	Sample size at titrant strength, H_2O at 2 mg/mL, (g)
0.2	2 to 5
0.5	0.8 to 4
1.0	0.4 to 2
1.5	0.25 to 1.5
>3.0	0.2 to 0.4

Karl Fischer Oven

- Corn oil
- DDG
- Isolates sample in sealed vial
- Low maintenance
- Can be automated
- Saves cost on reagents



Oven Method Step by Step

- Conditioning before each determination
- Blank value of empty sample vial
- Absolute amount of water in the range of hundreds of µg
- Nitrogen or other dry and inert gas as carrier gas
- Temperature gradient to define optimal oven temperature
- Oven method can be fully automated

Quality Control

Water Standards:

- 0.1% or 1% recommended for coulometric
- 1% recommended for volumetric

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Questions?