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Avoiding Common Pitfalls in Karl Fischer Analysis

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Outline

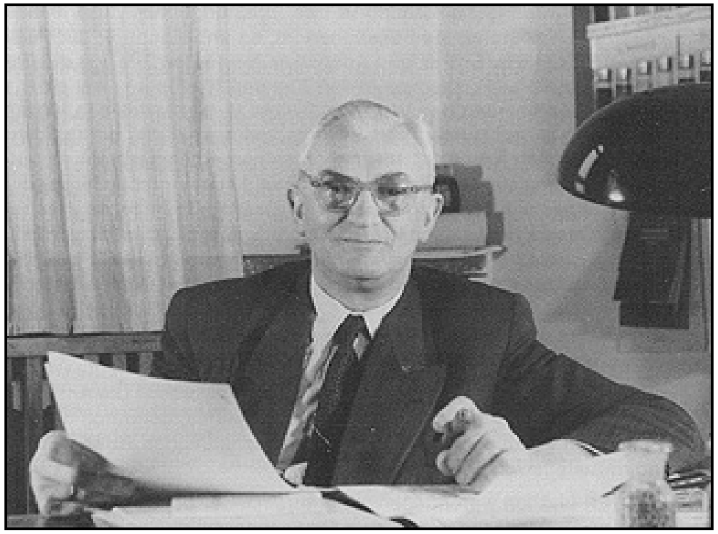
- What in Karl Fischer Analysis?
- Overview of Karl Fischer Analysis
  - Volumetric
  - Coulometric
  - Water standards
- Common Pitfalls in Karl Fischer Analysis
  - What they are
  - How to avoid or over come them
- Summary
- Conclusion

What is Karl Fischer Analysis?

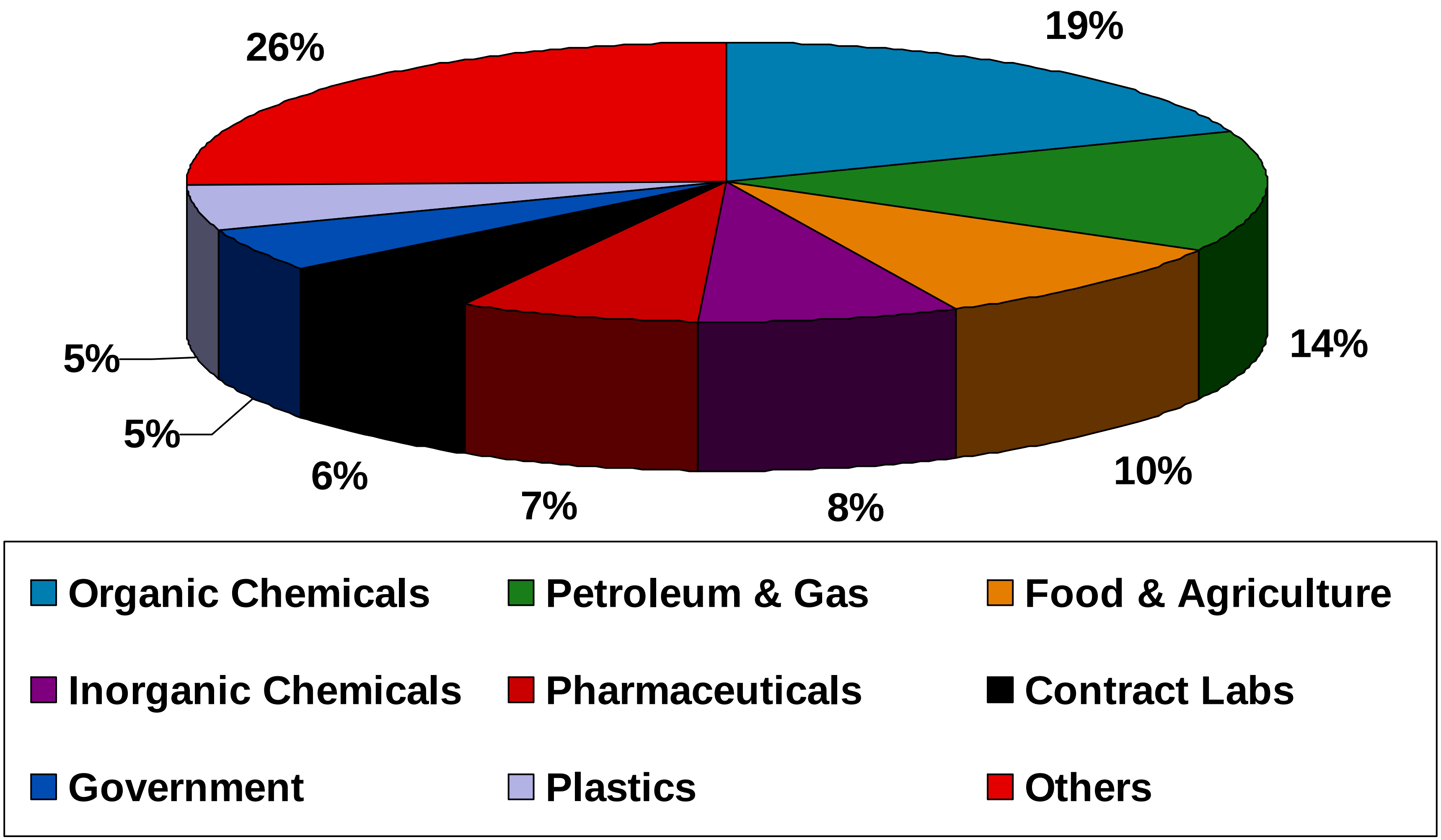
- Karl Fischer analysis (KF) is a popular titration-based analytical technique used in R&D, QC, and Manufacturing to quantify water content in a variety of products

- Named after the German petroleum chemist who discovered it in the 1930's

- Basic principle: a 1:1 reaction between water and an Iodine-containing reagent



Where is Karl Fischer Analysis Used?



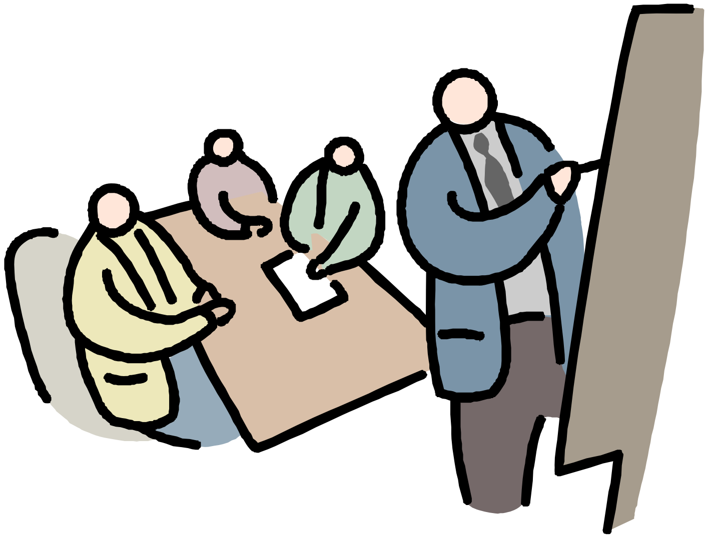
Are There Alternatives to KF?

Method	Advantage	Disadvantage
Loss on Drying (LOD)	Less expensive	Not specific for water
Gas Chromatography (GC)	None	Expensive Time consuming Low water content only
Distillation	None	Lower accuracy Time consuming Need large samples sizes
Nuclear Magnetic Resonance (NMR)	None	Expensive Time consuming
Infrared Spectroscopy (IR)	None	Expensive Lower accuracy Interpretation issues

Comparative Advantages of KF

- Selective for water
- High accuracy and precision
- Small sample quantities
- Easy sample preparation
- Short analysis duration
- Nearly unlimited measuring range
- Independent of sample's state of matter
- Independent of presence of other volatiles
- Suitable for automation

Overview of Karl Fischer Analysis

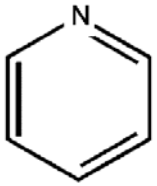


Basic Principles of KF

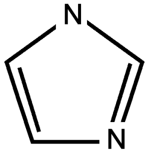
- KF reaction proceeds according to the following 2-step mechanism:
  - $CH_3OH + SO_2 + RN \rightarrow [RNH]SO_3CH_3$
  - $[RNH]SO_3CH_3 + \boxed{I_2 + H_2O} + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2\ [RNH]I$
- Or in English:
  - Sulfur dioxide reacts with an alcohol (in this case, Methanol) to form an ester intermediate which is neutralized, or buffered, by the base (RN)
  - The subsequent oxidation of the alkylsulfite salt to an alkylsulfate salt by Iodine consumes Water in a 1:1 ratio to Iodine

Required Components of KF Reagent

- Based on the KF reaction mechanism, the reagent needs to contain the following:
  - Alcohol
    - Originally used: Methanol
    - Now used: Methanol, Ethanol, 2-MEO, DEGME, DEGEE, etc.
  - Base
    - Originally used: Pyridine
    - Now used: Imidazole
  - Iodine
  - Sulfur dioxide

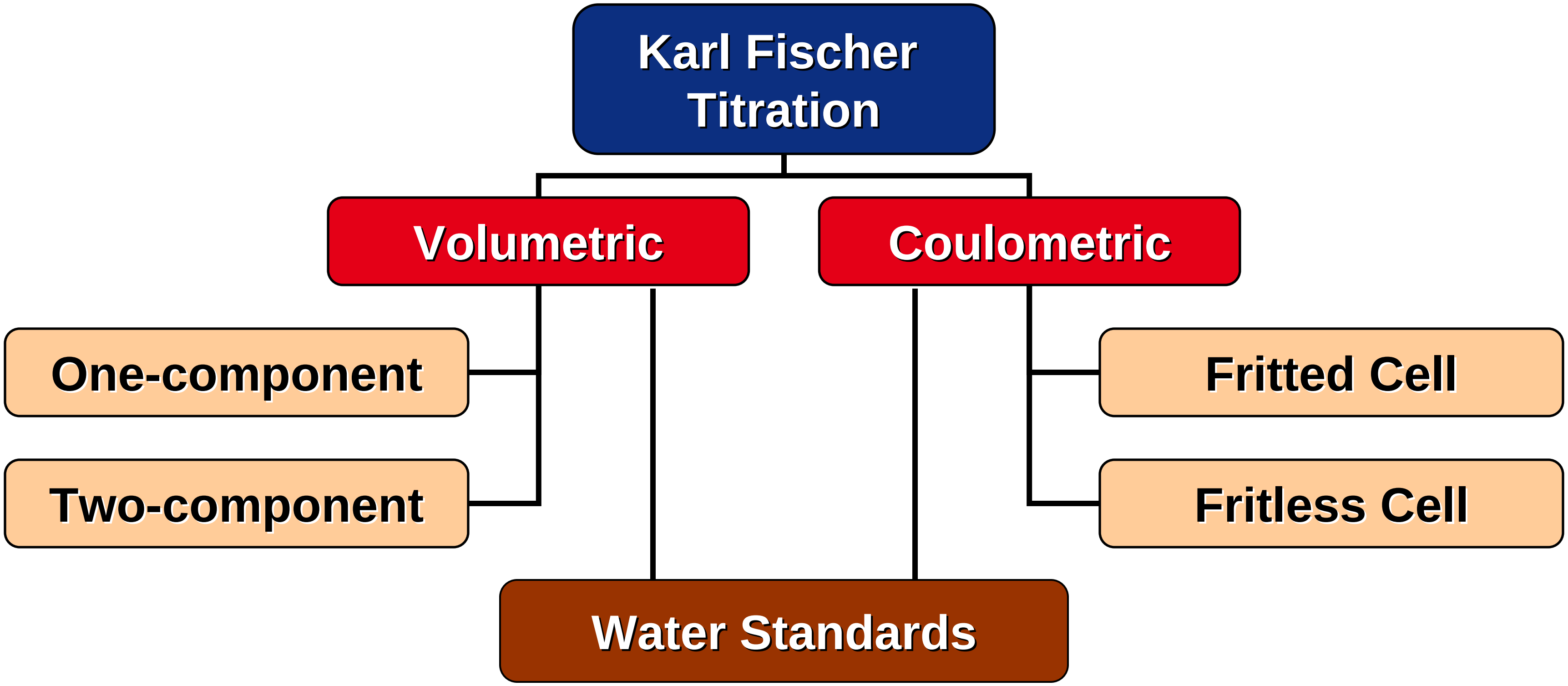


PYRIDINE



IMIDAZOLE

Karl Fischer Titration Types



Karl Fischer Titration

Volumetric

Coulometric

One-component

Two-component

Fritted Cell

Fritless Cell

Water Standards

Types of KF Analysis

- **Volumetric KF**
  - For high water content samples
- **Coulometric KF**
  - For low water content samples
- **Indirect KF**
  - Uses an evaporator in conjunction with <u>either</u> a volumetric or a coulometric titrator when certain sample solubility or reactivity issues prevent direct analysis

Volumetric KF Analysis

- Iodine-containing titrant is added mechanically by the titrator’s burette during titration
- Water is quantified on the basis of the volume of KF reagent consumed
- Best suited for water content range of: **100 ppm to 100%**

One-Component vs. Two-Component Volumetric Reagents

One-Component System

- Titrating Reagent

  (CombiTitrant, Composite)
  - Iodine
  - Sulfur dioxide
  - Imidazole
  - Suitable alcohol
- Solvent
  - Methanol (typically)
  - Special formulations for challenging sample matrices
    - Oils, Fats, Ketones, etc.

Two-Component System

- Titrating Reagent

  (Titrant)
  - Iodine
  - Methanol
- Solvent
  - Sulfur dioxide
  - Imidazole
  - Methanol (typically)
  - Special formulations for challenging sample matrices
    - Oils, Fats, etc.

One-Component vs. Two-Component Volumetric Reagents

- One-Component System (B)

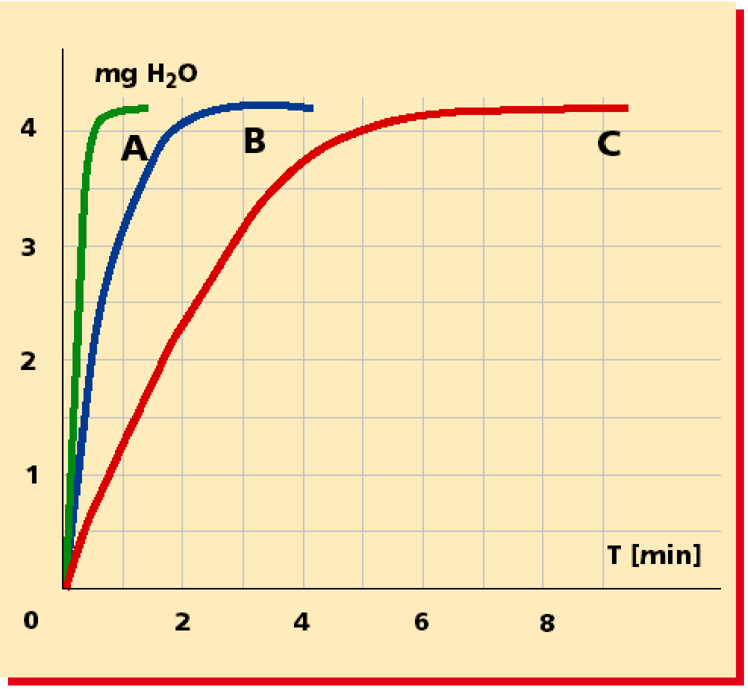
ex: CombiTitrant 5 + CombiMethanol

  - High accuracy
  - Simpler to use
  - Fewer working medium changes
  - LESS EXPENSIVE

- Two-Component System (A)

ex: Titrant 5 + Solvent

  - Highest accuracy
  - Faster titration time
  - Sharper endpoint
  - More stable titer
  - MORE EXPENSIVE



- Karl Fischer's Original System (C)

ex: Pyridine-based KF Reagent + Methanol

  - Slow
  - Sluggish endpoint

Titration Speed vs. Precision

SPEED

- The larger the burette, the faster the titration
  - Titer (mg/mL) x burette volume (mL)
- Example for CombiTitrant 5
  - 5 mL burette = 25 mg/min
  - 10 mL burette = 50 mg/min
  - 20 mL burette = 100 mg/min

PRECISION

- Smallest increment as a function of burette resolution (1/10,000th of burette volume)
- For example
  - 5 mL burette = 0.5 μL
  - 10 mL burette = 1.0 μL
  - 20 mL burette = 2.0 μL

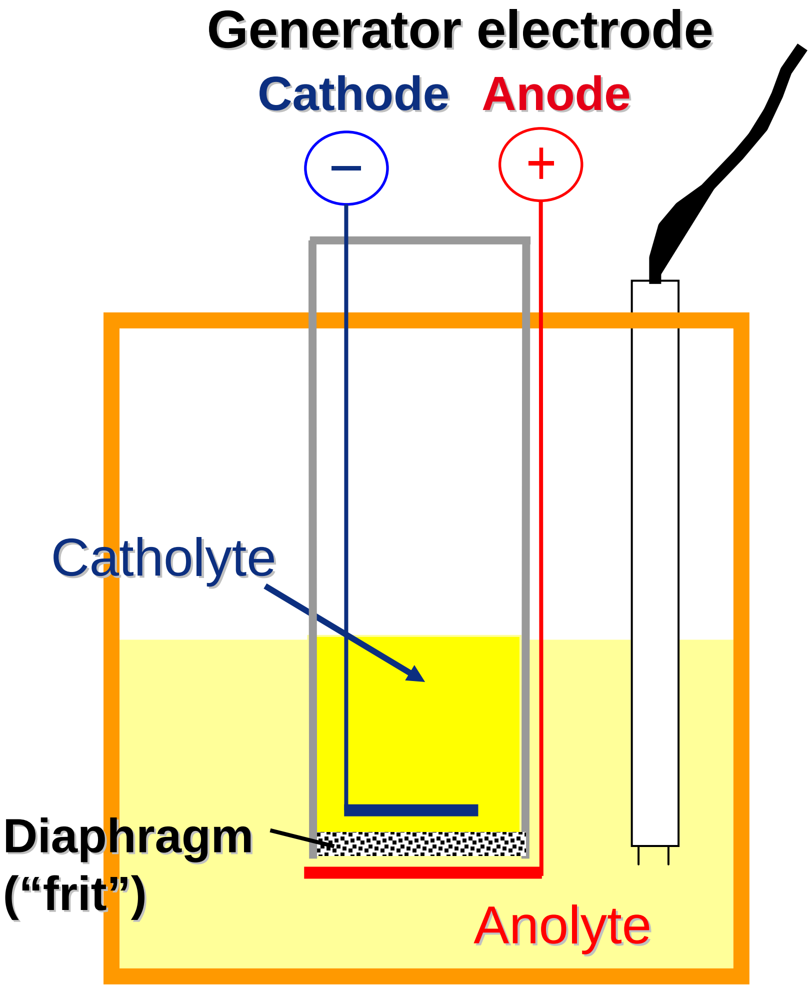
More About Titration Precision

- If a 1 g sample is titrated using a titrant with a titer of 5 mg/mL on a 5 mL burette, 1.0 µL represents 5 µg of water
  - 5 µg of water in 1 g sample = 5 ppm = 0.0005%
- Reproducibility is affected by the drift, sample type, availability of water, KF reaction kinetics, and endpoint determination method used
- Contributing factors
  - Atmospheric water contamination during sample introduction
  - Absorption of water by sample during handling
  - Sample losses during handling
  - Reliability of balance used for sample weighing

Coulometric KF Analysis

- Iodine is generated electrochemically in the KF reagent during titration
- Water is quantified on the basis of measuring current and time
- Best suited for water content range of: **1 ppm to 8%**

Conventional Coulometric Cell



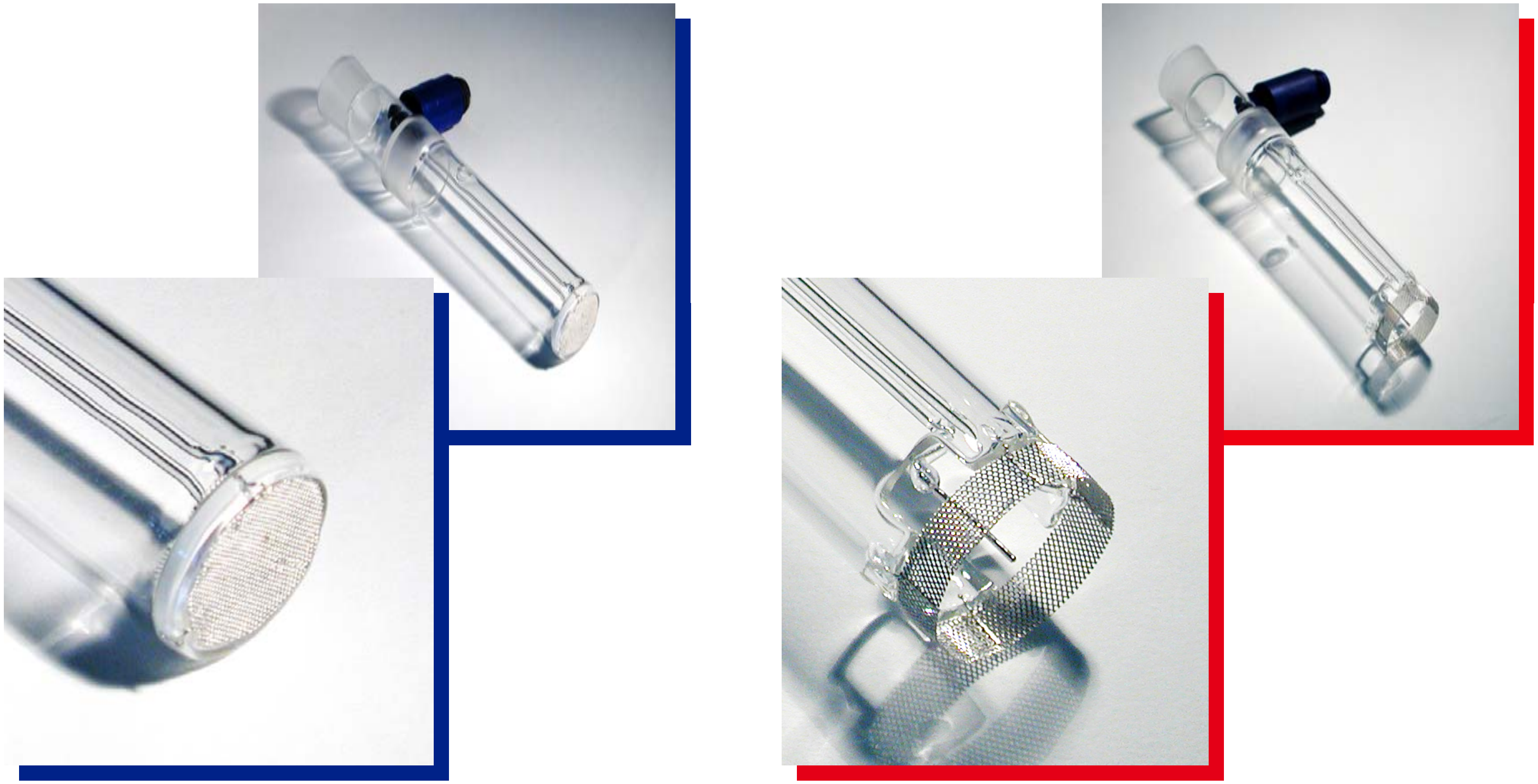
Indicator electrode
(double platinum pin electrode)

- Anolyte:
  Sulfur dioxide, Imidazole, Iodide, Methanol, co-solvents (as needed)
- Catholyte:
  similar (or modified) solution

What is a Frit?

- A diaphragm – or frit – separates the anode from the cathode that form the electrolytic cell known as the generator electrode
- The purpose of the frit is to prevent the Iodine generated at the anode from being reduced back to Iodide at the cathode
    - Instead of reacting with Water
- At one time all coulometric cells were fritted
- In 1989 an innovative cell was developed that through a combination of factors, but without a frit, made it nearly impossible for Iodine to reach the cathode and get reduced to Iodide

Fritted vs. Fritless Cells



The fritless cell has different electrode geometry

Advantages of a Fritless Cell

- Uses only one reagent
  - Lower cost
- Titration cell much easier to clean
  - Reduced downtime
- Long-term drift (background) value more stable
  - Use reagent longer without refilling
- Refilling of electrolyte suitable for automation
  - Reduced downtime
  - Increased lab safety

Volumetric vs. Coulometric KF

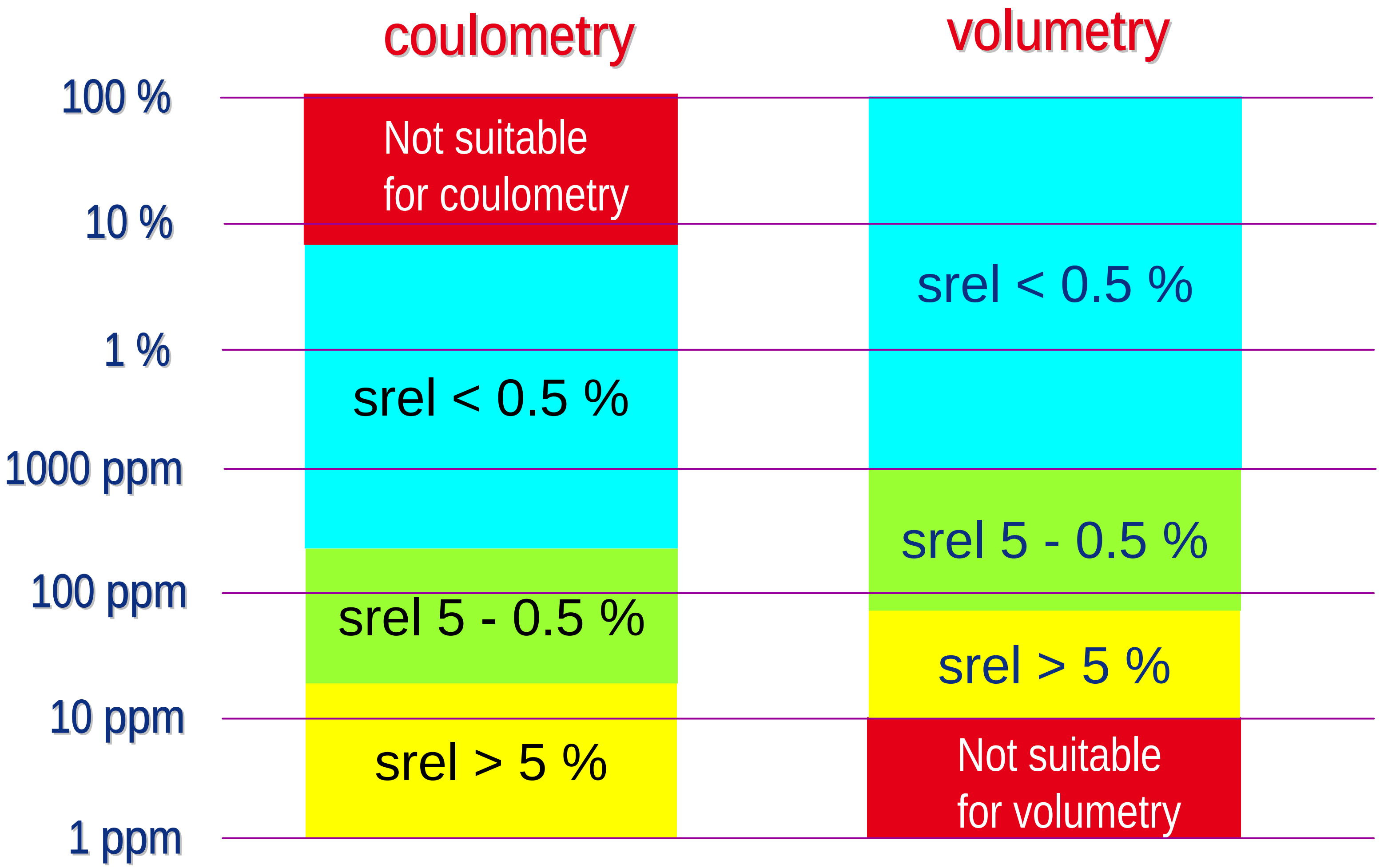
Volumetric KF

- Practical range of water content
  - 100 ppm to 100%
- Titration rate
  - Up to 50 mg/min
- Suitable sample types
  - Solids, liquids, gases
- Less sensitive to interfering side reactions

Coulometric KF

- Practical range of water content
  - 1 ppm to 8%
- Titration rate
  - Up to 2 mg/min
- Suitable sample types
  - Liquids, gases
  - Direct addition of solids to coulometric cell not recommended

Water Content and KF Reproducibility



coulometry

volumetry

100 %

10 %

1 %

1000 ppm

100 ppm

10 ppm

1 ppm

Not suitable for coulometry

srel < 0.5 %

srel 5 - 0.5 %

srel > 5 %

srel < 0.5 %

srel 5 - 0.5 %

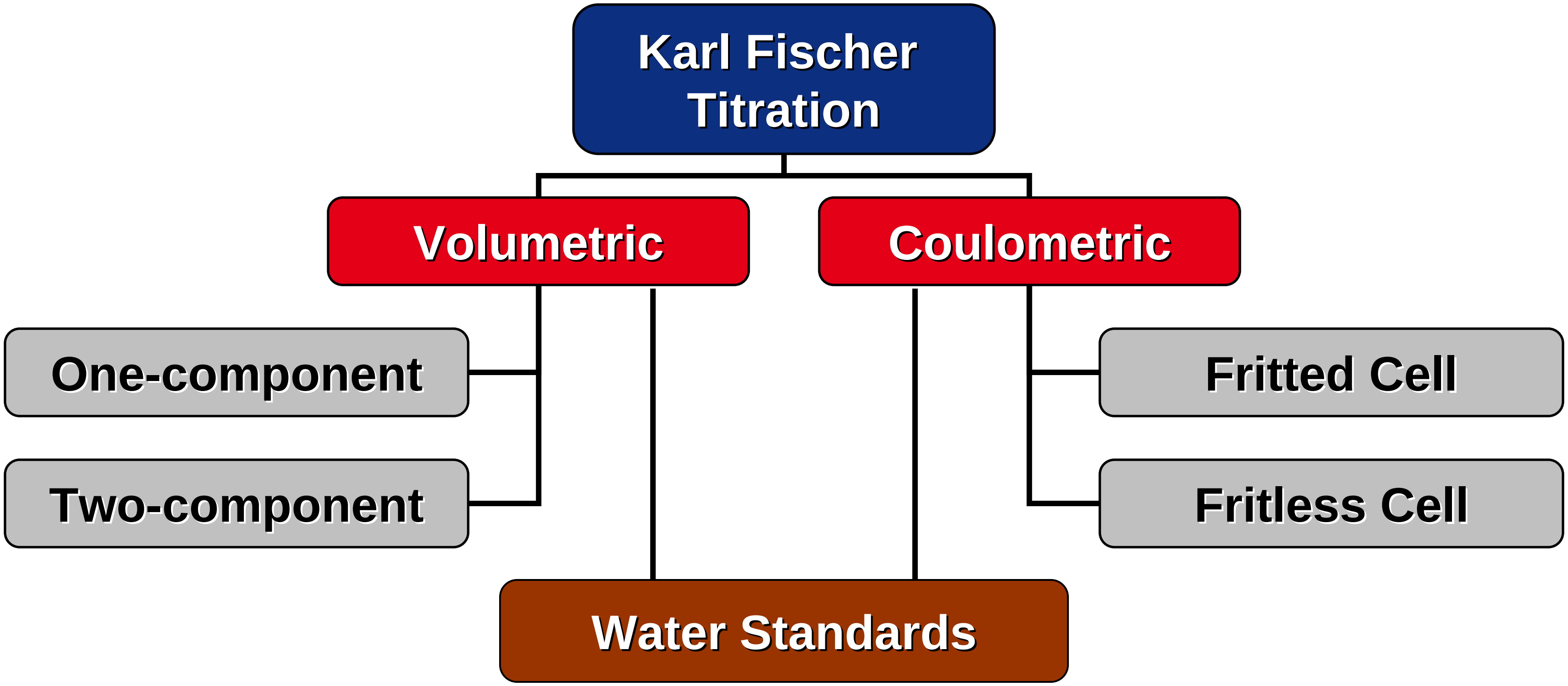
srel > 5 %

Not suitable for volumetry

Control & Validation Procedures in KF

- Volumetric KF
  - Titer ("factor") determination
  - Performance control (titer check)
  - Result verification
- Coulometric KF
  - Performance control
  - Result verification

Standards for Karl Fischer Titration



Karl Fischer Titration

Volumetric

Coulometric

One-component

Two-component

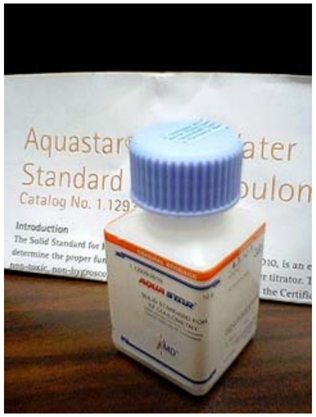
Fritted Cell

Fritless Cell

Water Standards

Standards Applicable to Volumetric KF

- Solid standards:
  - Sodium Tartate Dihydrate
    - form: powder for enhanced solubility
    - expiration dated: 48 months
    - water content: 15.66%
    - sample size: 0.05-0.15 g (max. solubility in 50 mL Methanol)
  - Lactose Monohydrate
    - form: powder for enhanced solubility
    - expiration dated: 24 months
    - water content: 5.0%
    - sample size: 0.30-0.60 g



Standards Applicable to Volumetric KF

- Liquid standards:
  - Water Standard 1% NIST
    - traceable to NIST SRM 2890
    - form: 10 x 8 mL sealed ampoules
    - expiration dated: 60 months
    - water content: 1.0% (10,000 ppm)
    - sample size: 2.0-3.0 g
  - 100% Water
    - not recommended:
      - must use <u>extremely</u> small sample size (10-50 µL)
      - high sampling error
      - variable quality, no traceability

Accuracy and Precision of Volumetric KF Standards

Material	Nominal Water	Mean Water	Relative Std Dev
Water	100%	100.04%	1.05%
Sodium Tartrate Dihydrate Solid Standard	15.66%	15.51%	0.78%
Ampoulized Liquid Standard 1%	1.00%	1.00%	0.09%
Ampoulized Liquid Standard 0.1%	1000 ppm	997 ppm	0.58%

Standards Applicable to Coulometric KF

- Liquid standards only:
  - Water Standard 0.1% NIST
    - traceable to NIST SRM 2890
    - form: 10 x 8 mL sealed ampoules
    - expiration dated: 60 months
    - water content: 0.1% (1000 ppm)
    - sample size: 1.0-2.0 g
  - Water Standard 0.01% NIST
    - traceable to NIST SRM 2890
    - form: 10 x 8 mL sealed ampoules
    - expiration dated: 60 months
    - water content: 0.01% (100 ppm)
    - sample size: 2.0-5.0 g

Accuracy and Precision of Coulometric KF Standards

Material	Nominal Water	Mean Water	Relative Std Dev
Ampoulized Liquid Standard 0.1%	1000 ppm	1003 ppm	0.6%
Ampoulized Liquid Standard 0.01%	100 ppm	105 ppm	1.1%

Water Standards Usage Tips

- When using solid standards, make sure that they are fine powders
  - Cheaper, coarsely ground materials will not dissolve completely
- When using low-moisture liquid standards pre-dry glass syringes in a desiccator
  - Never use plastic syringes with 1000 ppm and 100 ppm standards
- Determine all sample sizes by weight rather than volume
  - Use four or five-decimal place analytical balances
- In volumetry, use sufficient sample to have the burette dispense 1/3 to 1/2 of its volume
  - Minimizes any errors due to poor burette resolution

Common Pitfalls in Karl Fischer Analysis

“Potential Pitfalls” = Sources of Error

- Choice of equipment
- Sample size
- Preparation of titration cell
- Sample weighing technique/equipment
- Sample transfer technique
- Sample introduction into titration cell
- Sample-reagent issues
  - Sample reactivity
  - Sample solubility
  - Sample pH issues

Choice of Equipment

- Potential pitfalls, such as …
  - Volumetric instruments have poor reproducibility in the very low water content range
  - Coulometric instruments have poor reproducibility in the very high water content range
  - Reactive or hard-to-dissolve samples may not provide accurate results using direct analysis

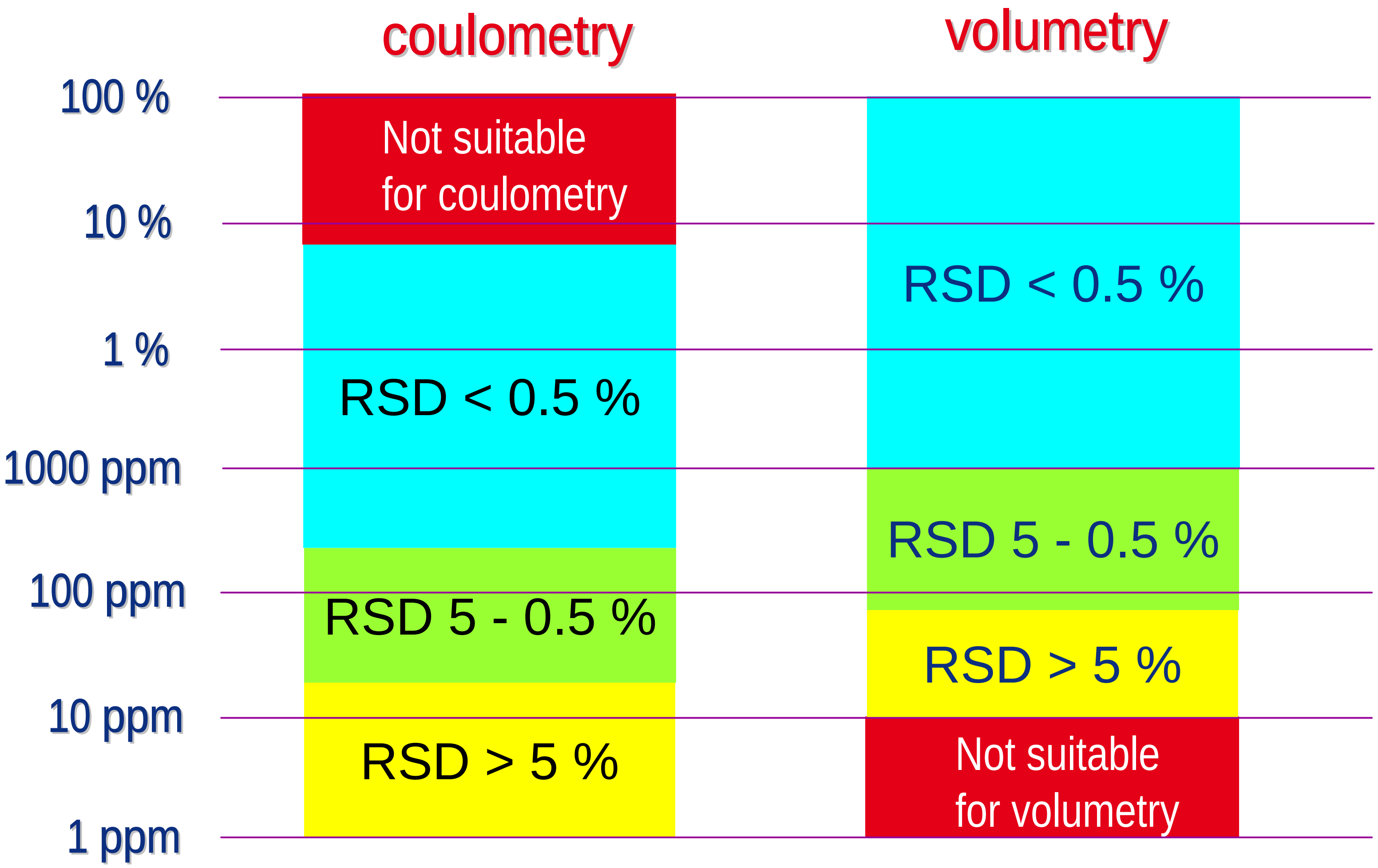
Choice of Equipment

- For high water content (1000ppm - 100%)
  - Use a **volumetric** titrator

- For low water content (0.5ppm [10µg] - 8%)
  - Use a **coulometric** titrator

- If sample dissolves poorly and/or gives side reactions which cannot be overcome by specialized reagents
  - Use an **Oil Evaporator** in conjunction with titrator

Water Content and KF Reproducibility



coulometry

volumetry

100 %

10 %

1 %

1000 ppm

100 ppm

10 ppm

1 ppm

Not suitable for coulometry

RSD < 0.5 %

RSD 5 - 0.5 %

RSD > 5 %

RSD < 0.5 %

RSD 5 - 0.5 %

RSD > 5 %

Not suitable for volumetry

Sample Size

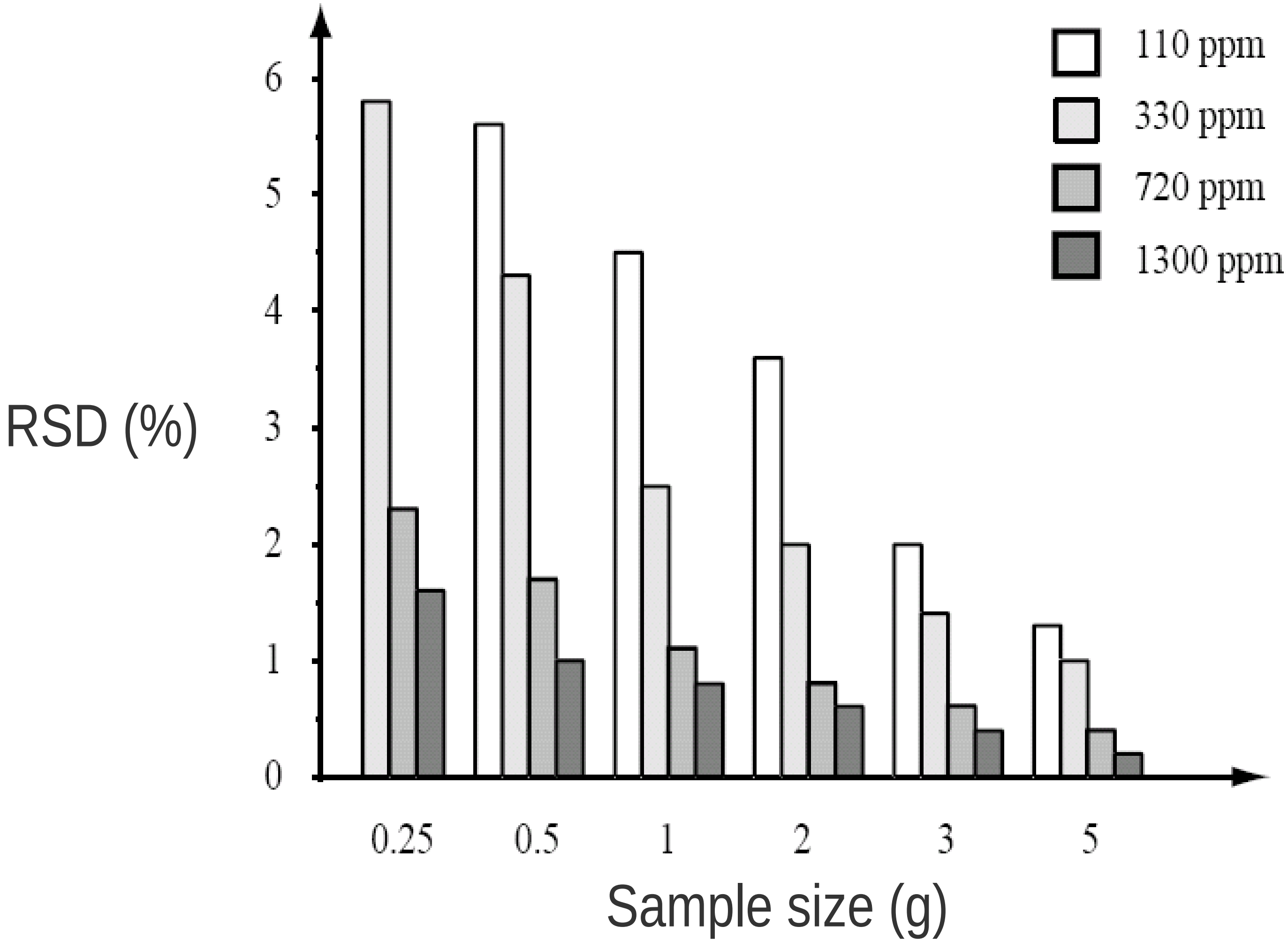
- Potential pitfalls, such as …
  - Sample size required for reproducible volumetric analysis of samples with very low water content is often unrealistically high
    - Leads to solubility issues and waste of reagent
  - Sample size required for reproducible coulometric analysis of samples with very high water content is often unmanageably low
    - Leads to difficulties with accurate sample weighing, handling, and transfer

Recommended Sample Size for KF

SAMPLE WATER CONTENT	VOLUMETRIC SAMPLE SIZE	COULOMETRIC SAMPLE SIZE
100%	0.02 to 0.05 g	NOT RECOMMENDED
50%	0.05 to 0.25 g	0.01 g
10% (100,000 PPM)	0.25 to 0.50 g	0.01 to 0.05 g
5% (50,000 PPM)	0.50 to 2.50 g	0.05 to 0.10 g
1% (10,000 PPM)	2.50 to 5.00 g	0.10 to 0.50 g
0.5% (5,000 PPM)	5.00 to 7.50 g	0.20 to 1.00 g
0.1% (1,000 PPM)	7.50 to 10.0 g	1.00 to 2.00 g
0.01% (100 PPM)	10.0 to 15.0 g	2.00 to 5.00 g
0.001% (10 PPM)	15.0 to 20.0 g	5.00 to 10.0 g
0.0001% (1 PPM)	NOT RECOMMENDED	10.0 g OR MORE

Remember: sampling error is inversely proportional to sample size

Effect of Sample Size on RSD



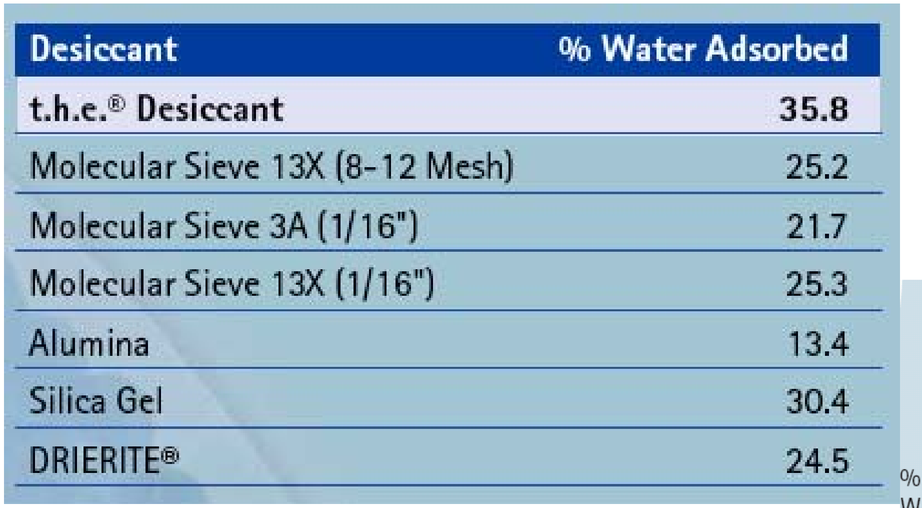
Preparation of Titration Cell

- Potential pitfalls, such as …
  - Dirty titration cell glass from accumulated sample residue
    - Leads to contamination of subsequent samples
  - Accumulated sample residue on indicator/generator electrodes
    - Leads to low accuracy due to insulation of electrodes
  - Septa with many or large puncture holes
    - Lead to contamination of titration cell with atmospheric moisture resulting in high and/or drift (background) values
  - Old, saturated desiccants in drying tubes
    - Lead to contamination of titration cell with atmospheric moisture resulting in high and/or drift (background) values

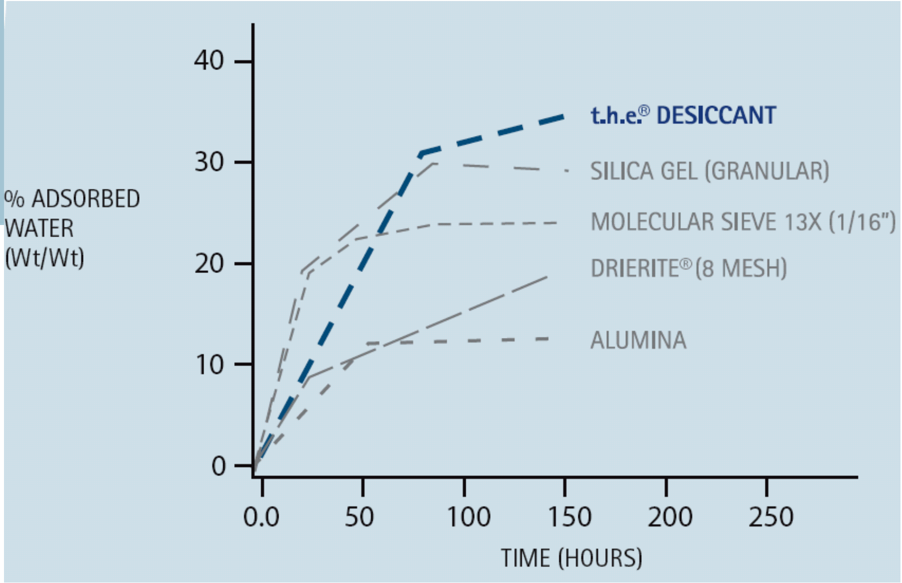
Preparation of Titration Cell

- Clean cell and electrodes using hot water
  - Rinse with methanol when using methanol-containing reagents
  - Rinse with acetone when using methanol-free reagents
- Use septa free of holes
- Use fresh desiccant in drying tubes
- Make sure cell is dry by rinsing interior of cell with dry reagent
- Make sure background is low and solvent is at a stable endpoint

Desiccants for KF Drying Tubes



Desiccant	% Water Adsorbed
t.h.e.® Desiccant	35.8
Molecular Sieve 13X (8-12 Mesh)	25.2
Molecular Sieve 3A (1/16")	21.7
Molecular Sieve 13X (1/16")	25.3
Alumina	13.4
Silica Gel	30.4
DRIERITE®	24.5

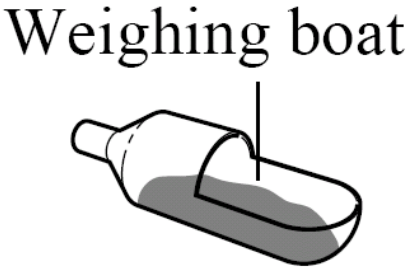


Sample Weighing

- Potential pitfalls, such as …
  - Use of non-analytical balances
    - Leads to inconsistent results
  - Improper sample transfer devices can result in sample mass loss between balance and titrator and splatter in the titration cell
    - Leads to inaccurately high results
  - Moisture may condense on balances in labs without humidity controls
    - Leads to inaccurately high results

Sample Weighing

- Use a four or five point analytical balance
- Choose a weighing vessel with a small opening
- For liquid samples
  - Use syringes for most liquids
  - Disposable transfer pipettes
- For powder samples
  - Manufacturer supplied samplers
  - Cut-off disposable 3ml plastic syringes
  - Cut-off transfer pipette bulbs

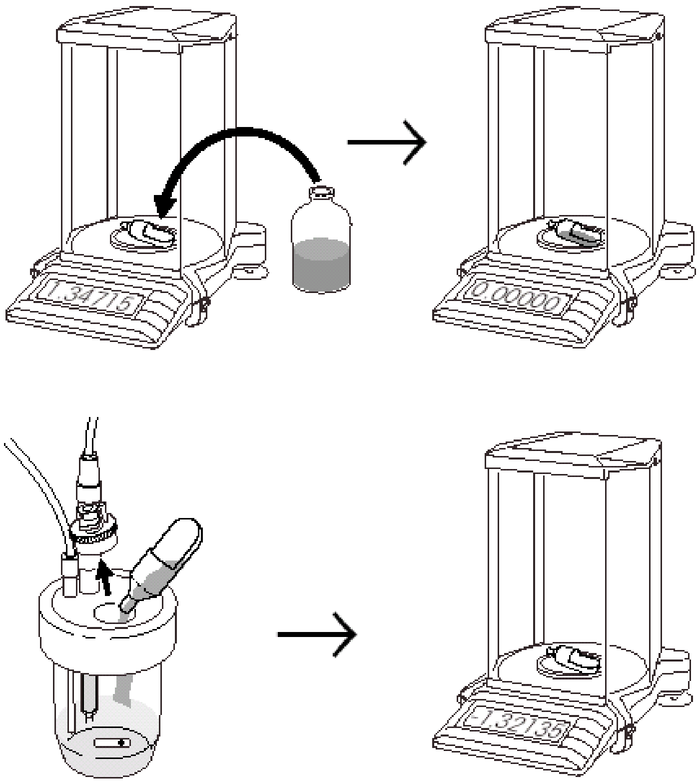


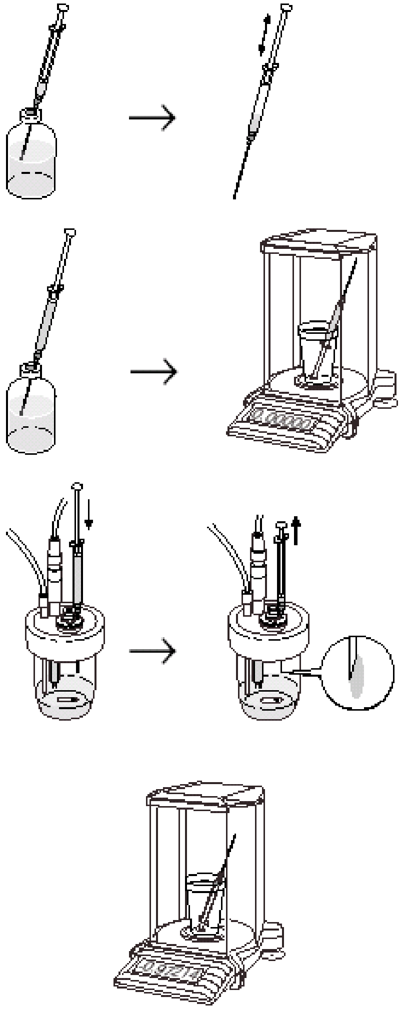
Sample Weighing

- Place the syringe in the middle of the weighing pan
- Wait until balance is stabilized before recording weights

- Choose an optimum sample size
  - For volumetric titration, use 1/3 to 3/4 volume of burette
  - For coulometric titration, sample should contain ~1000 µg H_2O

Weighing by Difference





Sample Transfer

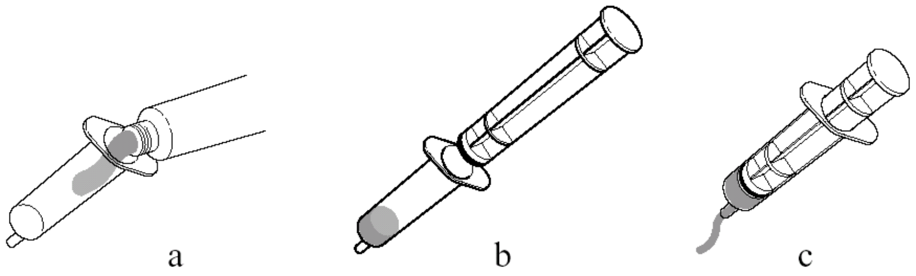
- Potential pitfalls, such as …
  - Non-homogenous and non-representative samples do not provide meaningful or consistent results
    - Leads to low accuracy and reproducibility
  - Poor transfer techniques can result in sample contamination with atmospheric moisture
    - Leads to inaccurately high results
  - Improper sample transfer devices can result in sample mass loss between balance and titrator and splatter in the titration cell
    - Leads to inaccurately high results

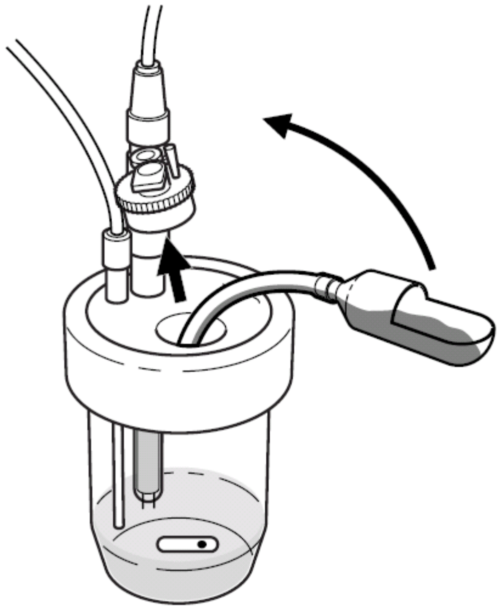
Sample Transfer

- Use a homogenous sample
- Use a representative sample
- Avoid contact with ambient moisture
  - at STP, 1ft^3 of air contains 20 mg H_2O
- Use a glove box for hygroscopic samples

Transfer of Problematic Samples

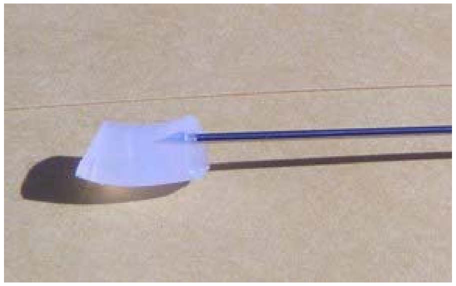
- Highly Viscous Samples
  - Heavy oils, greases, etc.
  - Difficult to push through syringe needles
- Fine Powder Samples
  - Minerals, free-flowing salts, etc.
  - Tend to stick to sample port, electrodes, titration cell walls

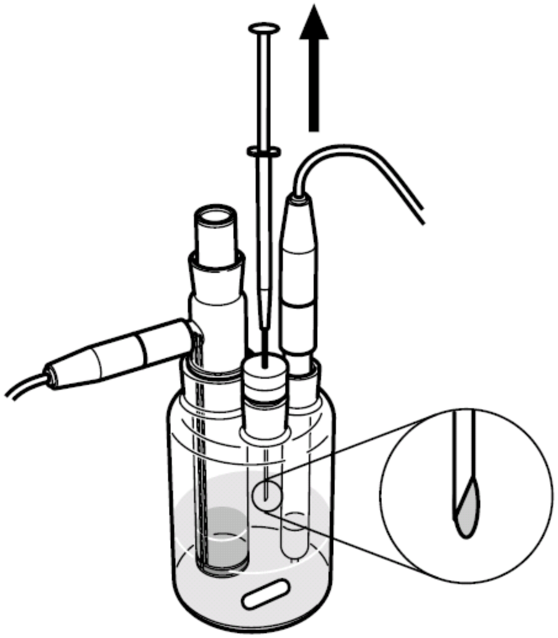




Sample Introduction to the Titration Cell

- Use a fresh septum for the injection port
- Dry syringes in a desiccator
- Rinse the syringe with the sample
- Add sample above liquid level in cell
- Seal the needle tip with a silicone rubber
- Avoid sample sticking to the inner vessel
- Pull back last drop at needle tip





Sample Reactivity Issues with Fuels

- Certain fuel additives are reactive and are known to interfere with KF titration
  - Modified mercaptans
  - Higher phenols
  - Ketoacids
  - Polysiloxanes
  - Metal oxides

Sample Reactivity Issues with Fuels

- Contaminants and by-products in fuels, especially spent fuels, can interfere with KF titration
  - By-products of incomplete combustion
  - PCBs
  - Trace metals
  - PAHs
  - Gasoline

Compounds Reactive with Iodine

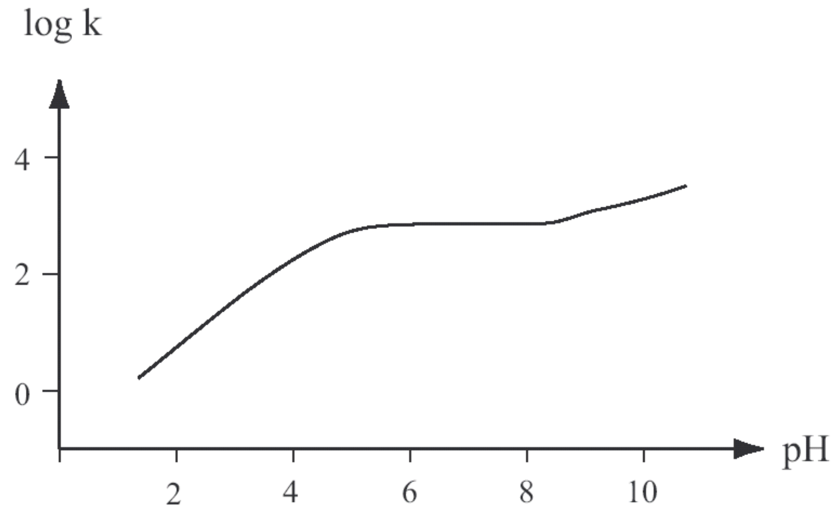
- Ascorbic acid
- Arsenites $[AsO_2]^-$
- Arsenates $[AsO_4]^{3-}$
- Boric acid
- Tetraborates $[B_4O_7]^{2-}$
- Carbonates $[CO_3]^{2-}$
- Disulfites $[S_2O_5]^{2-}$
- Iron (III) salts
- Hydrazine + derivatives
- Hydroxides $[OH]^-$
- Hydrogen carbonates $[HCO_3]^-$
- Copper (I) salts
- Mercaptans/thiols [RSH]
- Nitrites $[NO_2]^-$
- Oxides: CaO, MgO, MnO_2
- Peroxides [ROOR]
- Selenites $[SeO_3]^{2-}$
- Silanol $[R_3SiOH]$
- Sulfites $[SO_3]^{2-}$
- Tellurites $[TeO_3]^{2-}$
- Thiosulfates $[S_2O_3]^{2-}$
- Tin (II) salts

Testing for Reactivity with Iodine

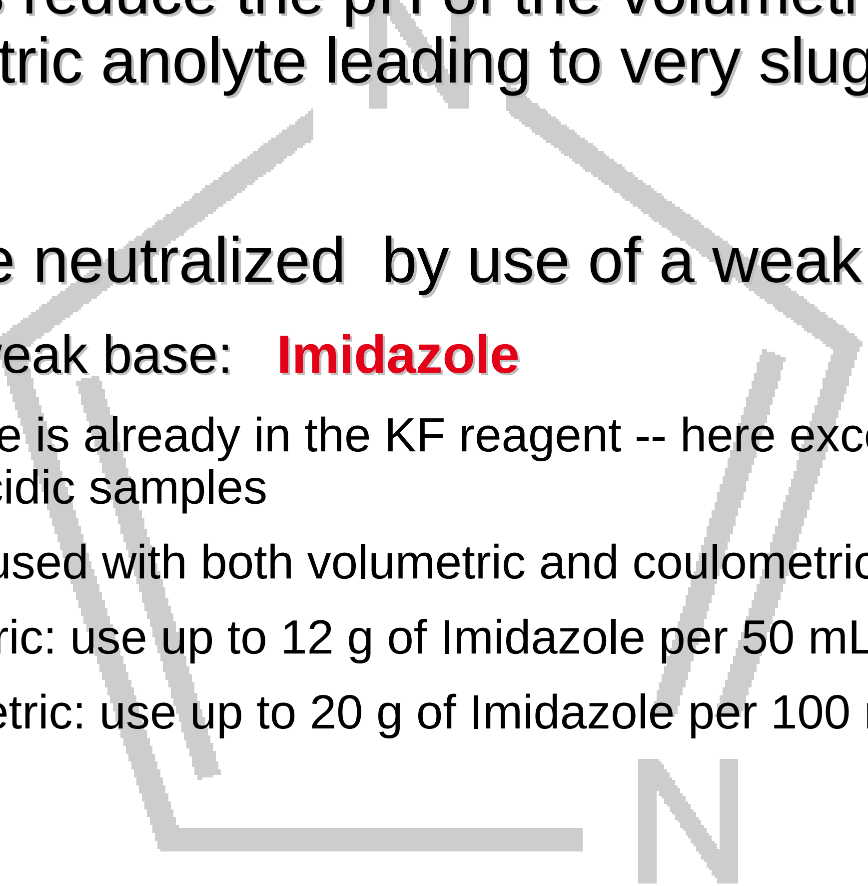
- Simple procedure
  - Dissolve 1 to 2 crystals of Iodine in Methanol to produce a dark brown solution
  - Inject sample in question directly into this solution
  - Observe resultant coloration:
    - If no color change occurs, sample is not reactive with Iodine
    - **If a color change occurs, sample is reactive with Iodine**
- If sample is reactive with Iodine, direct titration is not possible
  - Use of Oil Evaporator is recommended
  - External extraction is an alternative if no evaporator available

KF of Acidic and Basic Samples

- pH between 5 and 8
  - Titration proceeds normally
- pH lower than 5
  - Titration speed is very slow
- pH higher than 8
  - Titration rate is fast due to interfering esterification side reaction which produces Water (vanishing endpoint)
- Highly acidic or basic samples need to be buffered to bring the overall pH in the range of 5 to 8



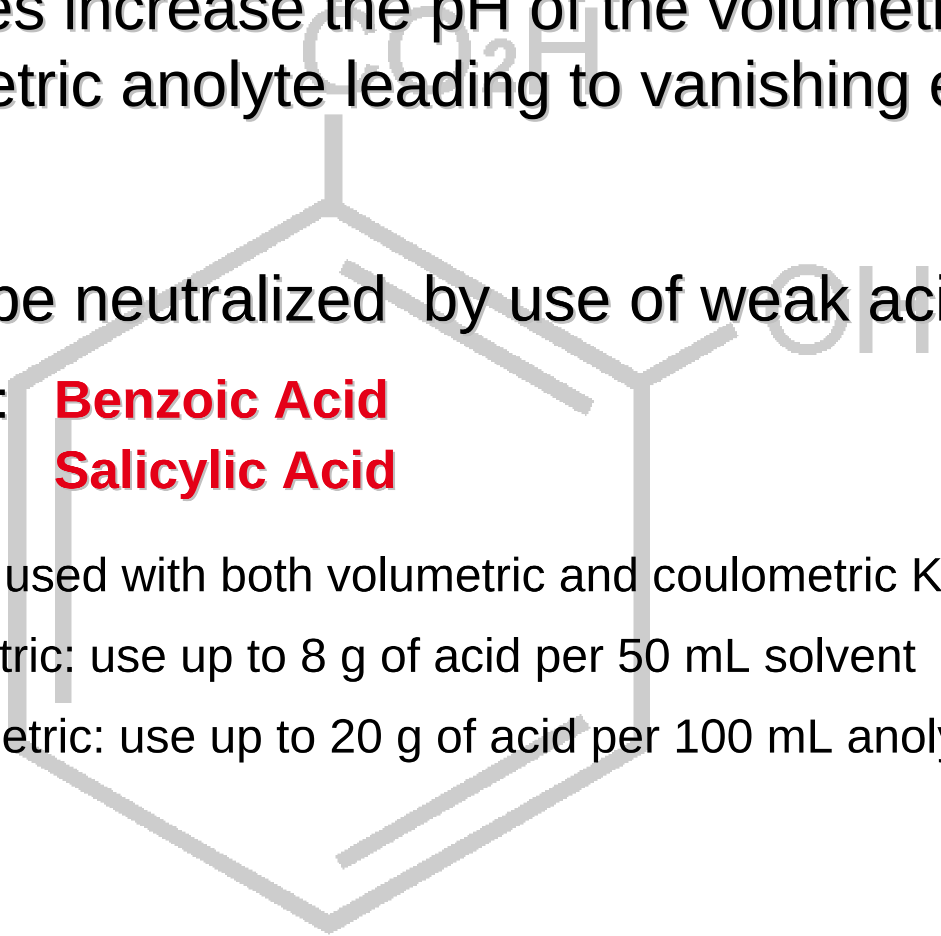
Buffering Acidic Samples



- Strong acids reduce the pH of the volumetric solvent or the coulometric anolyte leading to very sluggish titrations

- Acids can be neutralized by use of a weak base
  - Optimum weak base: **Imidazole**
    - Imidazole is already in the KF reagent -- here excess of it is added to buffer acidic samples
    - Can be used with both volumetric and coulometric KF titration
    - Volumetric: use up to 12 g of Imidazole per 50 mL solvent
    - Coulometric: use up to 20 g of Imidazole per 100 mL anolyte

Buffering Basic Samples



- Strong bases increase the pH of the volumetric solvent or the coulometric anolyte leading to vanishing endpoints

- Bases can be neutralized by use of weak acids
  - Use either: **Benzoic Acid**
    Salicylic Acid
    - Can be used with both volumetric and coulometric KF titration
    - Volumetric: use up to 8 g of acid per 50 mL solvent
    - Coulometric: use up to 20 g of acid per 100 mL anolyte

Summary: Sources of Error

- Choice of equipment
- Sample size
- Preparation of titration cell
- Sample weighing technique/equipment
- Sample transfer technique
- Sample introduction into titration cell
- Sample-reagent issues

Conclusion

- Karl Fischer analysis is a widely accepted automated method for quantifying water routinely used in many industries
- Errors in KF analysis may arise from a variety of sources
- This presentation reviewed strategies and practical tips to minimize analysis errors

Thank you for your attention!

Questions …