The influence of conductivity on Karl Fischer titration

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Introduction

- The mechanism of the Karl Fischer reaction

KF reaction: Oxidation of alkyl sulphite

1) \( \text{ROH} + \text{SO}_2 + \text{RN} \rightleftharpoons [\text{RNH}]\text{SO}_3\text{R} \)

2) \([\text{RNH}]\text{SO}_3\text{R} + \text{I}_2,\text{I}_3^- + \text{H}_2\text{O} + 2 \text{RN} \rightarrow [\text{RNH}]\text{SO}_4\text{R} + 2 [\text{RNH}]\text{I} \)

Competing equilibria in KF solutions:

Hydrogen sulphite can be oxidized in addition to alkyl sulphite:

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\begin{align*}
\text{HSO}_3^- + \text{I}_2,\text{I}_3^- & \rightarrow \text{SO}_3^- + \text{HI} \\
\text{HSO}_3^- + \text{ROH} & \rightarrow \text{ROSO}_2^- + \text{H}_2\text{O} \\
\text{HSO}_3^- + \text{H}_2\text{O} + \text{base} & \rightarrow \text{ROSO}_2\text{O}^- + \text{SO}_4^{2-} + \text{B-SO}_3
\end{align*}
\]
**Introduction**

- The composition of Karl Fischer solutions

**Main Components**

- \( I_2 \)
- \( SO_2 \)
- Base
- Solvent

**Determines**
- Stoichiometry
- Reaction rate
- Indication
- Dissolving properties

**For buffering**
- pH 5 – 8
- e.g. pyridine, imidazole

**For stable one component reagents:**
- Less reactive alcohol
  - e.g. DEGEE

**For optimum KF titration:**
- Reactive and polar alcohol
  - Methanol most suitable
Task
- Alternative solvents for methanol

Reagents for special applications
- for aldehydes & ketones (methanol free)
- dissolving properties adapted on samples
  e.g. addition of toluene, formamide, less polar alcohols

Reduction of toxic properties
- 2-methoxyethanol replaced by DEGEE
- substitution of methanol by ethanol or 1-propanol

without methanol:
observation overtitration, poor reproducibility
reasons ? lower reaction rate

indication problems !
The indication of the Karl Fischer titration
- principle

voltametrically or amperometrically
by polarizing a double platinum electrode

\[ \text{U[mV]} \]
\[ \text{U(stop)} \]
\[ \text{t[s]} \]

excess of \( I_2/I_3^- \) leads to strong decrease of the resistance (voltage) at the endpoint

anode: \( 2 I^- \rightarrow I_2 + 2 e^- \)
cathode: \( I_2 + 2 e^- \rightarrow 2 I^- \)
The indication of the Karl Fischer titration - influence of the solvent

electrochemical behaviour of KF solutions

- standard potential $E(I_2/I^-)$
- conductivity

1-propanol, $c(I_2) = 6 \times 10^{-4}$ mol/L

methanol, $c(I_2) = 6 \times 10^{-4}$ mol/L

Parameter $I(pol) - E(stop)$ adjusted on the solvent
one component titration
- comparison of the course of conductivity

start: low titration rate

no reactive components with fresh solvent

low reaction rate

low conductivity

titration: titration rate increases

addition of reagent

reaction rate increases

conductivity increases
Titration with different one component reagents and methanol

- Comparison of the course of conductivity

Type of solvent and base influence conductivity.
one component titration
- comparison of the course of conductivity

Titration with CombiTitrant 5 and several solvents

if indication problems:
adjust instrument parameters or composition of reagents

titration not possible
**one component titration**
- adjustment of composition of solvents

**to increase conductivity of solvents**

- addition of salts e.g. $R_N^+Br^-$

**use of diluted KF solvents**
- e.g. CombiSolvents, low concentrations of $SO_2$ and base

**advantages:**
- acceleration of reaction rate
- increased initial conductivity

ethanolic solvent for titrations with CombiTitrant (contains $SO_2$ and base)
one component titration
- adjustment of composition of solvents

water determination in oils & fats

- addition of toluene, chloroform, long chained alcohols
- solvent mixtures of less polarity
- consider influence on indication

Diluted KF solvents for one component titration of oils & fats

CombiSolvent oils for mineral oils
- contains toluene

CombiSolvent fats for food industry
- contains butyl acetate and decanol
Two component titration based on methanol and ethanol

start:
reactive components in KF solvent ensure optimum conditions

titration:
almost constant conductivity

ethanol:
conductivity decreases (factor 3 to methanol)
**Coulometry**

* - influence of conductivity

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**generation of iodine!**

**indication of the endpoint**

conductivity more important than for volumetry

conductivity of catholyte (cell with frit) or working medium (fritless cell) decreases during determination

long chained alcohols, xylene or chloroform can be added

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**with diaphragm**

addition of max. 40 % / volume to CombiCoulomat frit

higher robustness

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**without diaphragm**

addition of max. 20 % / volume to CombiCoulomat fritless

high current at generator electrode

limit 5-6 mS/cm before current breaks down
Coulometry
- development of new reagents

goal ➔ increased conductivity
  especially for reagents for fritless cell

reached by ➔ addition of salts

problems ➔ solubility
  side reactions, stability
  formation of agglomerates

development activities in progress
Conclusion

A minimum conductivity is necessary for indicating the endpoint of KF titration.

replacement or reduction of methanol:

- consider influence on indication
- solvent determines \( E(I_2/I_3^-) \) and conductivity

adjustment of instrument parameters and/or compositions of reagents are necessary

e.g. advantage of diluted KF solvents for one component titration (apura CombiSolvents)

development of coulometric reagents with increased conductivity