Good Titration Practice™
in Surfactant Titration
Dear Reader

Surfactants and detergents are an integral part of our daily life and play an important role in industry processes. The analysis of anionic, cationic or non-ionic surfactant concentration in formulations, raw products, liquid detergents, cosmetic products, lubricants, cooling emulsions etc. is an important quality criterion in production.

The composition of those products is constantly improved in order to cope with increasing performance demands. As a result the composition has become more complex and consequently the titration analysis far more demanding. A particular challenge is the selectivity required to accurately titrate an active surfactant within a complex sample matrix. Therefore well-selected and aligned analytical equipment consisting of an appropriate titrator and a dedicated surfactant sensor are required – one of the essential requirements in Good Titration Practice™ to ensure result quality.

The application power of the METTLER-TOLEDO potentiometric surfactant sensors DS800-TwoPhase and DS500 as well as the DP5 Phototrode™ for colorimetric titrations can only be fully exploited with the Excellence titrators. The available method parameters are self-explaining and offer the right granularity for optimization in order to cope with the various sample matrices of the large variety of surfactant-containing products.

It is with pleasure that we present to you this unique and comprehensive application brochure that provides essential information on different analytical techniques used for surfactant analysis.

We wish you great success and enjoyment in surfactant titration

Hans-Joachim Muhr
Market Support Manager
BA Titration

Rolf Rohner
Marketing Manager
BA Titration
# Contents

1 **SURFACTANT TITRATION AT A GLANCE** ................................................................. 4  
   1.1 General information on sample and procedure ................................................. 4  
   1.2 Properties of surfactants ..................................................................................... 5  
   1.3 Chemical reaction ............................................................................................... 5  
   1.4 Surfactant titration ............................................................................................. 6  

2 **BASICS OF SURFACTANTS** ............................................................................ 7  
   2.1 Definition ........................................................................................................... 7  
   2.2 Types of surfactants ........................................................................................... 8  
   2.3 Surfactants in finished products and formulations .......................................... 11  

3 **OVERVIEW OF THE TITRATION TECHNIQUES** ............................................. 12  
   3.1 Turbidimetric titration ....................................................................................... 12  
   3.2 Colorimetric two-phase titration ....................................................................... 12  
   3.3 Potentiometric titration in the aqueous phase ................................................. 12  
   3.4 Potentiometric two-phase titration .................................................................... 12  
   3.5 Comments ......................................................................................................... 12  

4 **TURBIDIMETRIC TITRATION** ......................................................................... 13  
   4.1 Principle ............................................................................................................ 13  
   4.2 Shape of titration curves ................................................................................... 13  
   4.3 Tips & hints ....................................................................................................... 14  
   4.4 Results of turbidimetric titration ....................................................................... 15  

5 **COLORIMETRIC TWO-PHASE TITRATIONS** .................................................. 17  
   5.1 Principle ............................................................................................................ 17  
   5.2 Classical two-phase titration ............................................................................. 17  
   5.3 Automation of classical two-phase titration ...................................................... 17  
   5.4 Tips and hints .................................................................................................... 19  
   5.5 Results of automated colorimetric two-phase titration .................................... 20  

6 **POTENTIOMETRIC TITRATIONS IN AQUEOUS PHASE** ......................... 21  
   6.1 Principle ............................................................................................................ 21  
   6.2 Potentiometric SSE titration: Profile of titration curves ................................... 22  
   6.3 Practical Hints ................................................................................................. 22  
   6.4 Results of potentiometric titrations in aqueous phase ..................................... 23
7 POTENTIOMETRIC TWO-PHASE TITRATIONS ................................................. 24
  7.1 Principle ................................................................................................................24
  7.2 Potentiometric two-phase titration: tips and hints .................................................25
  7.3 Results of potentiometric two-phase titrations ......................................................26

8 CHEMICAL REACTIONS IN SURFACTANT TITRATION................................. 27
  8.1 Anionic/cationic surfactants ..................................................................................27
  8.2 Nonionic surfactants .............................................................................................28
  8.3 Amphoteric surfactants ........................................................................................29

9 SURFACTANT TITRATION: COMPARISON OF DIFFERENT TECHNIQUES 30
  9.1 Titer determinations with standard solutions ........................................................30
  9.2 Recovery tests with SDS and CPC solutions .......................................................30
  9.3 Anionic content determination in formulated products .........................................31

10 CONCLUSIONS ................................................................................................ 34
  10.1 Automated colorimetric two-phase titration (2P): ..............................................34
  10.2 Turbidimetric titration: .......................................................................................34
  10.3 Potentiometric techniques: SSE and nonaqueous titration ..............................34

11 LITERATURE .................................................................................................... 35
# 1 Surfactant titration at a glance

## 1.1 General information on sample and procedure

<table>
<thead>
<tr>
<th>Nature of the sample</th>
<th>Nature of the sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Raw materials or finished products, formulated products</td>
<td><strong>Qualitative</strong> composition: Which surfactants?</td>
</tr>
<tr>
<td></td>
<td><strong>Quantitative</strong> composition: What is their expected content?</td>
</tr>
<tr>
<td></td>
<td>• Additional components and their content: Salts, fragrances, alcohol, water.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>• What is the analytical procedure used?</td>
<td>• Information on actual procedure is crucial</td>
</tr>
<tr>
<td>• If different surfactants are present: Possible interferences?</td>
<td></td>
</tr>
<tr>
<td>• pH value of the sample solution: Possible interferences?</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample preparation:</th>
<th>Sample preparation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Finished and formulated products: Separation of components before titration?</td>
<td></td>
</tr>
<tr>
<td>• pH value: pH-adjustment to avoid interferences</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample/Titrant</th>
<th>Sample/Titrant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample: Anionic surfactants</td>
<td>Titrant e.g.:</td>
</tr>
<tr>
<td></td>
<td>• Hyamine® 1622</td>
</tr>
<tr>
<td></td>
<td>• CPC</td>
</tr>
<tr>
<td></td>
<td>• DDMICl</td>
</tr>
<tr>
<td>Sample: Cationic surfactants</td>
<td>• SDS</td>
</tr>
<tr>
<td></td>
<td>• DOSS (dioctyl sodium sulfosuccinate)</td>
</tr>
<tr>
<td>Sample: Nonionic surfactants</td>
<td>• Sodium tetraphenylborate (Na-TPB), with BaCl₂ as activator</td>
</tr>
<tr>
<td>Sample: Amphoteric surfactants (e.g. amidobetaines)</td>
<td>• Na-TPB</td>
</tr>
<tr>
<td></td>
<td>• NaOH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method parameters</th>
<th>Method parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Potentiometric two-phase titration (DS800)</td>
<td>• DYN e.g. 0.02-0.2 mL, dE(set)=8 mV</td>
</tr>
<tr>
<td></td>
<td>• EQU e.g. dE/dt = 1 mV/2s</td>
</tr>
<tr>
<td></td>
<td>t_{min} = 5 s, t_{max} = 30 s</td>
</tr>
<tr>
<td></td>
<td>• Evaluation: Standard (if necessary: asymmetric)</td>
</tr>
<tr>
<td>• Potentiometric titration (DS500)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Colorimetric 2P-titration (DP5)</td>
</tr>
<tr>
<td></td>
<td>• INC e.g. 0.15 mL</td>
</tr>
<tr>
<td></td>
<td>• Signal acquisition: Mix time e.g. 5 s, Separation time e.g. 40 s</td>
</tr>
<tr>
<td>• Turbidimetric titration (DP5)</td>
<td>• INC e.g. 0.1 mL</td>
</tr>
<tr>
<td></td>
<td>• EQU e.g. dE/dt = 1 mV / 1 s</td>
</tr>
<tr>
<td></td>
<td>t_{min} = 3 s, t_{max} = 15 s</td>
</tr>
<tr>
<td></td>
<td>• Evaluation: Minimum or standard</td>
</tr>
</tbody>
</table>
1.2 Properties of surfactants
For detailed information, consult references [1] to [5], and in particular reference [4], where R. Schulz has extensively described many practical aspects concerning surfactant titration.

1.2.1 Surface active behaviour
- Migration and enrichment at solution interfaces and solid surfaces. (e.g., glass-water, water-air) ⇒ Avoid too many dilution steps.
- Heterogeneous concentration in glass flask, especially for low content.
- Enrichment of cationic surfactants on glass surfaces: the positive charge of cationic surfactants is attracted by the negatively polarised glass surface of a bottle due to the presence of silicates, -O-Si-O-. This leads to a lower concentration of titrants such as Hyamine® 1622, CPC and DDMICl in solution.

1.2.2 Foam formation
- Higher surfactant concentration in foam than in solution.
  → Avoid shaking and strong stirring during sample preparation.
  → Add few mL methanol or other alcohols to reduce foam (max. 5-10% v/v).

1.2.3 Micelle formation (self-aggregation)
- Strongly dependent on concentration (above critical micelle concentration).
- Surfactant molecules in micelles are not available for titration.
  They become available only after titration of molecules in solution.
  → Too fast a titration leads to lower results.
- Direct potential measurements (ISE) as e.g. for metal ions are generally not possible.

1.3 Chemical reaction
- Precipitation reaction (anionic, cationic, nonionic surfactants)
  The analyte has to be titrated with a counter-ionic surfactant leading to the precipitation of a titrant-analyte complex.
- Complete precipitation of the titrant-analyte complex:
  Surfactants molecules have non-polar alkyl chains of various lengths.
  Chain length > 12 carbon atoms (C12) ........... completely precipitated
  Chain length C8-C12 .................................. partial precipitation
  Chain length < 8 carbon atoms (C8) ............... difficult to titrate
- Titration speed
  A precipitation reaction requires the appropriate titration time:
  - do not titrate too fast
- Solubility product of the analyte-titrant complex formed:
  It depends on the alkyl chain length of the analyte.
  In general, a shorter alkyl chain length leads to higher solubility.
- Endpoint indication:
  The precipitation reaction leads to
  - a potential change (potentiometric indication),
  - an increase in turbidity (turbidimetric/photometric titration), or
  - to a color change (photometric indication) when indicators are used.
1.4 Surfactant titration

1.4.1 Titrant preparation

- Choice of the appropriate counter-ionic titrant to ensure a complete precipitation reaction.
  For instance, longer alkyl chains and bulky ions such as DDMICl can lead to better results due to improved titration curves with respect to CPC and Hyamine®1622.

- When preparing a titrant solution, foam is always formed in the volumetric flask. This can be reduced by addition of a few mL ethanol (max. 3-5 mL) just before finishing filling up to the graduation mark: first, a 1 L volumetric flask is filled up to e.g. 980 mL with water. Foam is formed, which does not allow for the final addition of water exactly to the mark. 3-5 mL ethanol is added. As a consequence, foam is eliminated and the graduation mark is clearly visible. The last 20 mL water is added up to the mark.

- Cationic surfactant molecules cover a glass surface forming a layer. When preparing a fresh titrant solution of a cationic titrant (e.g. CPC), leave the solution e.g. over night to allow for saturation of the glass surface of the flask. Time is needed to reach saturation of the glass surface.

1.4.2 Sample size

General rule: avoid too small a sample size (lower content).
- Surfactants with many hydrophilic groups such as EO-units (-(CH₂-CH₂-O-)_n): increase sample size to improve precipitation
- Analyte with short alkyl chains and broad alkyl chain length distribution: increase sample size to improve precipitation

1.4.3 Chemical structure

- A surfactant is generally characterized by a broad distribution of alkyl chain lengths i.e. a specific amount of a surfactant contains molecules having alkyl chains with different lengths (e.g. from C₆ to C₁₂). For this, the molecular mass has to be understood as an average molecular mass.

- The number of polar groups (e.g., ethers or hydroxyl groups) affects the titration results since they affect the precipitation.

- The alkyl chain length affects the titration curve.

- Alkyl ether sulfates (anionics) with more than 10 EO-units has to be titrated as nonionic surfactants.

- The presence of nonionic surfactants can affect the analysis of ionic surfactants.

1.4.4 Additional interferences

- Salts affect the precipitation reaction: high salt concentration ⇒ flat titration curve (potentiometric detection)

- The influence of insoluble substances such as e.g. abrasive particles in tooth paste, can be decreased by adding methanol to the sample solution (5-10% v/v).

- Deionized water can contain molecules arising from the ion exchange cartridge material (e.g., sulfonates) and can lead to wrong content results. If necessary, a blank value determination has to be performed.
2 Basics of surfactants

2.1 Definition

Surfactant – surface active agent- (also called tenside) is the generic name for substances with a surface active behaviour i.e. they affect the surface tension of water by adsorbing at the liquid-gas interface, or they also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. They have a characteristic structure with one or more (non-polar) hydrophobic groups, and one or more (polar) hydrophilic groups i.e. groups which have no affinity and a strong affinity to water, respectively [ref. 1-5].

Due to the presence of polar and non-polar groups, surfactants are soluble in both organic solvents and water. The polar groups are soluble in polar solvents such as water, whereas non-polar groups are soluble in non-polar solvents such as chloroform. Their presence leads to a well-defined distribution of electrical charges within the chemical structure of a surfactant.

In aqueous solutions, the hydrophilic groups of the surfactant molecules are in contact with water, whereas the hydrophobic groups attempt to avoid water by emerging from the solution. Thereby they form a monomolecular layer that covers the surface of the solution.

Surface tension results from electrostatic interaction of neighbouring molecules forming the layer. Since the interaction between a surfactant and a water molecule is weaker than that between two water molecules, the surface tension of a surfactant solution is considerably reduced compared to water.
For this reason, surfactants increase the dissolving power of water for organic nonpolar substances (e.g. fat) and are therefore used as detergents in many applications. Soaps, i.e. the sodium (Na\(^+\)) or potassium (K\(^+\)) salts of fatty acids, are well-known examples of surfactants:

\[
\text{COO}^- \quad \text{Na}^+
\]

Sodium palmitinate, \(\text{C}_{15}\text{H}_{31}\text{COO-Na}\)

Additional examples
- Sodium stearate: \(\text{C}_{17}\text{H}_{35}\text{COO-Na}\)
- Sodium laurinate: \(\text{C}_{11}\text{H}_{23}\text{COO-Na}\)

When a specific concentration is exceeded, and the surface of a solution is completely covered, additional surfactant molecules form spheric aggregates: **micelles**. This concentration is called the **critical micelle concentration** (cmc). In a micelle, the hydrophilic groups build the surface of the sphere and the hydrophobic tails are oriented towards the center of the micelle. The hydrophobic center allows for the inclusion of non-polar molecules (Fig. 2).

### 2.2 Types of surfactants

Surfactants are classified according to the type and charge of the hydrophilic groups present in the molecule. We distinguish between four different classes of surfactants:

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polar hydrophilic head</strong></td>
<td>- electrical charge</td>
<td></td>
</tr>
<tr>
<td>Anionics</td>
<td>Negative charge(s)</td>
<td>(\text{C}<em>{17}\text{H}</em>{35}\text{COO-Na})</td>
</tr>
<tr>
<td>Cationics</td>
<td>Positive charge(s)</td>
<td>(\text{C}<em>{11}\text{H}</em>{23}\text{COO-Na})</td>
</tr>
<tr>
<td>Nonionics</td>
<td>No free ions in solution</td>
<td></td>
</tr>
<tr>
<td>Amphoterics (zwitterionics)</td>
<td>Both negative and positive electrical charges</td>
<td></td>
</tr>
</tbody>
</table>

Four different classes of surfactants

Among these surfactants, anionic (including soap) and nonionic surfactants are the most important, followed by cationics and amphoterics.

The advantage of nonionic surfactants is their high solubility at low temperature, which is ideal for laundry temperatures at about 30°C. Among nonionic surfactants, sugar-based alkylpolyglucosides (APG) have to be mentioned because they have become very relevant these days due to their production process starting from renewable materials.
Anionic Surfactants (negative electrical charge)

- Alkyl sulphate

\[ \text{H}_3\text{C} \quad \text{O} \quad \text{O} \quad \text{Na}^+ \]

Sodium laurylsulfate/Sodium dodecylsulfate, SDS (Wikipedia)

- Linear alkylbenzene sulphonate (LAS), e.g. \( \text{CH}_3\text{-(CH}_2\text{)}_{11}\text{-C}_6\text{H}_5\text{-SO}_3\text{^-Na}^+ \)

- Alkylbenzene sulphonate (ABS)

\[ \text{H}_3\text{C} \quad \text{O} \quad \text{S} \quad \text{Na}^+ \]

Sodium dodecylbenzenesulfonate (Wikipedia)

- Alkyl ether sulphate, e.g. \( \text{CH}_3\text{-(CH}_2\text{)}_{10}\text{-CH}_2\text{-O-(CH}_2\text{CH}_2\text{O)}_4\text{-SO}_3\text{^-Na}^+ \)

Sodium n-dodecyltetraethoxysulphate (Sodium laureth sulphate)

Cationic Surfactants (positive electrical charge)

- Alkyl pyridinium salts

\[ \text{n-Cetylpyridinium chloride (CPC, M = 340 g/mol)} \]

usually available as CPC monohydrate, M = 358.01 g/mol (Wikipedia)

- Quaternary ammonium salts

\[ \text{Benzethonium chloride (Hyamine® 1622, M = 448.10 g/mol),} \]

(Wikipedia)
• Imidazolium salts

\[
\text{DDMICl (1,3-didecyl-2-methyl-imidazolium chloride, } M = 399.10 \text{ g/mol) (www.sigmaaldrich.com)}
\]

• Fatty quaternary ammonium salts

\[
\text{CTAB (Cetyltrimethylammoniumbromide, } M = 364.45 \text{ g/mol) (Wikipedia)}
\]

Nonionic Surfactants (no free ions in solutions)

• Ethoxylated alkylphenols

\[
\text{Nonylphenol ethoxylate (Wikipedia)}
\]

• Alkyl polyethyleneglycols, e.g.

\[
\text{CH}_3\text{-(CH}_2\text{)_{10}-CH}_2\text{-O(CH}_2\text{CH}_2\text{O)}_9\text{H}
\]

Dodecanol 9-mole ethoxylate (1 EO unit: -CH}_2\text{CH}_2\text{O-}

Amphoteric Surfactants

• Amidobetaines

\[
\text{Cocamidopropylbetaine (Wikipedia)}
\]

• Alkyl ammonium sulphonates

\[
\text{N-Tetradecyl-N,N-dimethyl-3-ammonium-1-propane sulphonate (Wikipedia)}
\]
Usually, surfactant molecules have not a single specific alkyl chain (e.g., C\textsubscript{12}), but they are characterized by a distribution of alkyl chains of various lengths. For instance, betaines contained in commercial products such as shower foams and shampoos contain alkyl chains which can vary between C\textsubscript{8} and C\textsubscript{18} [4].

The number of EO-units (i.e., \(-\text{CH}_2\text{-CH}_2\text{-O}-\)) can also vary between e.g. 7 and 9 in ethoxylated alkylphenols. Thus, the indicated molecular mass M of a surfactant has usually to be understood as a weighted average value of the molecular masses of the components with various alkyl chains.

### 2.3 Surfactants in finished products and formulations

The typical composition of formulated products, of which the analyses are documented in this brochure, is given below. The composition was indicated by the producers, and/or it was given onto the label. Cationic surfactants are seldomly used and were not amongst the analysed products.

<table>
<thead>
<tr>
<th>Product</th>
<th>Composition</th>
<th>Anionics</th>
<th>Nonionics</th>
<th>Cationics</th>
<th>Amphoteric</th>
<th>Other components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shower foam</td>
<td></td>
<td>✓</td>
<td>(✓)</td>
<td>✓</td>
<td></td>
<td>Water &gt; 40-50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Additional components (^1)</td>
</tr>
<tr>
<td>Liquid detergents</td>
<td></td>
<td>✓</td>
<td>(✓)</td>
<td></td>
<td>✓</td>
<td>Water &gt; 40-50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Additional components (^2)</td>
</tr>
<tr>
<td>Liquid dishwasher</td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>Water &gt; 40-50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Additional components (^3)</td>
</tr>
<tr>
<td>Washing powder</td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>Water &lt; 40-50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fatty acids</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Additional components (^4)</td>
</tr>
<tr>
<td>Toothpaste (gel)</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td>Water &lt; 20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Additional components (^5)</td>
</tr>
</tbody>
</table>

\(^1\) low percentages: perfumes, dyes, stabilizers, cellulose derivatives and salt (viscosity), alcohol.

\(^2\) low percentages: perfumes, dyes, stabilizers, salt (viscosity), alcohol.

\(^3\) low percentages: perfumes, dyes, skin protective substances.

\(^4\) low percentages: perfumes, enzymes, builders, borates, silicates, phosphates, carbonates.

\(^5\) low percentages: amine fluorides, polyglucosides, silica, titanium dioxide, phosphates, cellulose, fluorine.

This table has to be considered as an indicative table. Detailed information can be found in references [1-5]. Note that each product has its specific formulation, and the composition includes more than one class of surfactants, and additional substances (salts, fragrances,...).

Generally, these components affect the analysis, and thus interferences can not be excluded. For this reason, appropriate choice of pH value and sample preparation, e.g. separation of the components or chemical modifications, can be necessary [see ref. 1-5].

For instance, too low a pH can lead to protonation of betaines (in particular, of their carboxylic group, \(-\text{COO}^\ldots\text{H}^+\)). The protonated betaines can partially neutralize the anionic analyte in the sample leading to a lower result [see ref. 4].
3 Overview of the titration techniques

3.1 Turbidimetric titration
The turbidity of an aqueous or mixed phase sample solution is measured using a DP5 Phototrode™. It measures the light transmission through the sample. Near the equivalence point, a precipitate between titrant and analyte is formed, and the solution becomes turbid. The equivalence point is at the minimum in light transmission (Evaluation: «Minimum»).

However, if the signal does not show a clear minimum and is noisy, the curve is evaluated at the largest change in turbidity (Evaluation: «Standard»). In this case, the curve obtained from the standardization of the titrant must also be evaluated with the standard evaluation.

3.2 Colorimetric two-phase titration
To determine the anionic (cationic) surfactant content in a water/chloroform two-phase medium [1-3], the color change of a mixed indicator is monitored [6, 7]. The analyte is titrated with a counter-ionic surfactant, e.g. anionic surfactants are titrated with cationic surfactants (Hyamine®1622, CPC or DDMICl). After each increment addition, the mixture is stirred vigorously and then allowed to separate. An anionic-cationic, non-polar complex is formed and extracted into the organic phase (chloroform), where the light transmission is measured. At the equivalence point, the color of the organic phase changes from pink (blue) to blue (pink) leading to a sudden change in light transmission. The curve is evaluated at the largest change (Evaluation: «Standard»). This particular sequence can be achieved with the titration method function «Titration (2-phase)» of Titration Excellence. An additional possibility is to skip the separation of the two immiscible liquid phases my measuring the light transmission under continuous stirring of the sample [8, 9].

3.3 Potentiometric titration in the aqueous phase
These titrations are indicated with a surfactant sensitive electrode (SSE). Generally, a SSE has a PVC membrane or consists of a graphite rod containing an ion carrier [1, 3-5]. The potential is formed by interaction between the ion carrier in the membrane and the analyte in the sample solution, and is measured against a reference electrode. During titration, the surfactant forms a non-polar complex which leads to a potential change giving an S-shaped curve to be evaluated with the «Standard» evaluation procedure. Amphoterics are also determined by potentiometry in a non-aqueous solvent with a pH glass electrode [10].

3.4 Potentiometric two-phase titration
A further development of the conventional SSE for the determination in aqueous solution is represented by probes which are chemically resistant to organic solvents. In this way, it is possible to monitor the potential change in a two-phase heterogeneous system consisting of an immiscible organic solvent and water. The DIN EN 14668, 14669 and 14680 standards describe the procedure in detail [11].

3.5 Comments
All techniques are mainly based on the formation of a non-polar complex between analyte and titrant. Following parameters must be considered to achieve correct results:

- Reaction speed: How long does it take to form the precipitate? The signal acquisition must consider the precipitation kinetics and thus, the appropriate parameters of the «Measure mode» (i.e. t(min), t(max) ,...) must be selected.

- Solubility/stability of the formed complex: The precipitation must be complete and –if possible- the complex must be insoluble.
4 Turbidimetric titration

4.1 Principle

Anionic (cationic) surfactants are titrated with cationic (anionic) surfactants. Near the equivalence point, a colloidal precipitate is formed, and the solution becomes turbid. In most cases, the precipitate dissolves again, due to titrant excess, and the turbidity is decreased again.

The colloidal precipitate leads to an increase in turbidity

4.2 Shape of titration curves

At the equivalence point, maximum turbidity is reached, and a minimum in light transmission is measured with a DP5 Phototrode™.

In most cases, the curves obtained have a well-defined minimum: the curve can be evaluated according to the «Minimum» procedure. On the right side, the titration curve of a titer determination of Hyamine®1622 using SDS as a reference material is shown.

However, some applications are also evaluated for the largest change in turbidity (Evaluation «Standard»), since the curves do not show a clear minimum, as in the case of the titer determination of SDS with CPC.

In this case, also the titer determination must be performed with the «Standard» evaluation procedure.
4.3 Tips & hints

4.3.1 pH value of the sample
The pH value of the sample solution affects the results. Depending on sample composition, the appropriate pH value has to be chosen to titrate the desired component.

Example: Liquid detergent containing anionic surfactants as well as fatty acids.

- Titration of sample at pH 3: anionic surfactants. Interferences due to fatty acids and amphoteric surfactants are avoided since at this pH value fatty acids are protonated, whereas amphoteric surfactants do not disturb. Thus, these components cannot be precipitated by addition of a cationic titrant (e.g. Hyamine®1622 or CPC).
- Titration of sample at pH 10: anionic surfactants and fatty acids.

4.3.2 Evaluation procedure
To select the appropriate evaluation, a test titration can be first performed without termination after the equivalence point. The titration will be run to the maximum termination volume. In this way, the whole profile of the titration curve is visible. This allows for the selection of the most appropriate evaluation parameter based on the curve profile.

4.3.3 Stirring
To achieve accurate and precise results, the following points should be taken into account:

- Avoid foaming of the sample,
- Appropriate dilution of the sample to avoid formation of a vortex
- Avoid inclusion of air bubbles into solution during stirring,
- Avoid adhering of air or water bubbles to the window or onto the mirror of the DP5 Phototrode™.

For these reasons, it is necessary select the appropriate stirring speed. Thus, select a medium to low stirring speed.

4.3.4 Cleaning and conditioning
During titration a precipitate is formed which covers

- the mirror coating of the DP5 Phototrode™,
  and
- the propeller stirrer.

Therefore, it is necessary to clean the DP5 Phototrode™ thoroughly after each sample with water or, if necessary, with ethanol. When using a sample changer, the introduction of a conditioning step after each sample can improve the cleaning efficacy.

4.3.5 Preparation of the DP5 Phototrode™
Before titration, it is necessary to follow these steps to achieve a stable transmission signal:

- Turn on the DP5 Phototrode™ and wait at least 15 minutes to obtain a stable signal.
- Adjust the mV reading to 1000 mV in deionised water by turning the knob on top of the DP5 Phototrode™.
4.4 Results of turbidimetric titration

In the following table, the anionic surfactant contents in different samples have been determined by titration with Hyamine®1622 [from 12]:

<table>
<thead>
<tr>
<th>Product</th>
<th>Surfactant component</th>
<th>Nominal value</th>
<th>Reference Value</th>
<th>No. of samples</th>
<th>Content</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid detergent 1</td>
<td>Average molar mass: M = 387</td>
<td>18.0</td>
<td>17.1 (pH 3)</td>
<td>5</td>
<td>17.24</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol ether sulfate</td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Secondary alkanesulfonate</td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cocamidopropylbetaine</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 2</td>
<td>Average molar mass: M = 362</td>
<td>38.5</td>
<td>32.8 (pH 3)</td>
<td>5</td>
<td>34.49</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol ether sulfate</td>
<td>11.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Secondary alkanesulfonate</td>
<td>20.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cocamidopropylbetaine</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nonionics (7 EO, M=520)</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 3</td>
<td>Average M=353.09</td>
<td>33.0</td>
<td></td>
<td>7</td>
<td>34.44</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Anionics A, M=346</td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anionics B, M=385</td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 4</td>
<td>Anionics as SDS, M=288.38</td>
<td>Lit.: 15-30</td>
<td>14.18 (pH 1-2)</td>
<td>5</td>
<td>14.32</td>
<td>1.56</td>
</tr>
<tr>
<td>Liquid dishwasher</td>
<td>Anionics as SDS, M=288.38</td>
<td>Lit.: 15-30</td>
<td>10-15</td>
<td>5</td>
<td>11.22</td>
<td>0.18</td>
</tr>
<tr>
<td>Shower foam 1</td>
<td>Na-Laurylethersulfate, M=430</td>
<td>15.0</td>
<td></td>
<td>7</td>
<td>15.01</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>Betaine, M=390</td>
<td>13.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Laurylethersulfate</td>
<td>Raw material, M=432</td>
<td>71.0</td>
<td></td>
<td>7</td>
<td>76.85</td>
<td>0.23</td>
</tr>
<tr>
<td>Washing powder 1</td>
<td>Anionics as SDS, M=288.38</td>
<td>-</td>
<td></td>
<td>6</td>
<td>7.28</td>
<td>2.22</td>
</tr>
<tr>
<td>Washing powder 4</td>
<td>Na-DBS, M=348.49</td>
<td>-</td>
<td></td>
<td>5</td>
<td>3.49</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>Fatty acids FA, M=274</td>
<td>3-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nonionics, M=740</td>
<td>4-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shampoo 1</td>
<td>Anionics as SDS, M=288.38</td>
<td>-</td>
<td></td>
<td>5</td>
<td>19.88</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Nonionics</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nominal value: The theoretical composition of the sample as total washing active matter. It is obtained by summing the percentages of all surfactant components.

Reference value: Value given by the producer and mostly based on classical colorimetric two-phase titration. It indicates the total washing active matter determined at a specific pH.

(n): Sample dissolved in water without any pH adjustment value.
General remarks:

- Various samples with different compositions have been measured. Where possible, the exact composition was obtained from the producers. Other information was found in the literature (e.g. average compositions based on OECD recommendations).

- Washing powders result in a turbid sample after dissolution, even when using a small sample size. The transmission signal is low and thus the appropriate threshold value and the sample size have to be selected.

- Washing powder 4:
  
  Sample preparation:
  - 3 g washing powder was dissolved in 100-200 mL warm water and subsequently diluted to 500 mL in a volumetric flask.
  - 20 mL aliquots have been titrated, and diluted to 50 mL with deionized water.
  - First, the pH value was adjusted to pH 3 before starting the titration of sodium dodecylbenzene sulfate (Na-DBS) with Hyamine®1622 as a titrant.
  - Subsequently, the pH was adjusted to pH 10 in order to titrate both fatty acids and Na-DBS with Hyamine®1622. The difference of both results gives the content of fatty acids.

  Note that the inverse procedure, i.e. first at pH 10 and subsequently at pH 3, did not lead to accurate results.

Although obvious, it is necessary to point out again that the turbidimetric titration can be successfully be performed only in sample solutions which are almost transparent and, where possible, colorless.

Therefore, aqueous solutions of anionic raw materials can be generally titrated by this technique.
5 Colorimetric two-phase titrations

5.1 Principle
The two-phase titration was first described by Epton in 1947 (For a review, see ref. [1-6]). It soon became a widely accepted method and was also developed to a standard method recognized by ASTM, BSI and DIN [7].

This method allows the determination of ionic surfactants by titration with a counter-ionic surfactant in a medium consisting of an aqueous (H₂O) and a chloroform (CHCl₃) phase.

For instance, anionics such as SDS can be titrated with cationics such as CPC, Hyamine®1622 or DDMICl (1,3-Didecyl-2-methyl-imidazolium-chloride). The equivalence point (EQP) of the titration is marked by a color change of the mixed indicator solution in the organic phase from pink to blue. The setup is illustrated in the picture on the right.

5.2 Classical two-phase titration
After addition of a titrant increment, the sample is stirred vigorously during a defined time period to allow reaction of the titrant with the analyte and its extraction into the organic phase (chloroform). The strong stirring is stopped and the two phases separate. This cycle is performed until a titrant excess leads to a clear colour change in the organic phase:

Addition of increment → Stirring → Separation of the two phases → Measure

5.3 Automation of classical two-phase titration
To fully automate the classical colorimetric two-phase titration, a special titration method function “Titration (2-phase)” is available in the Titration Excellence Line. This allows for the definition of suitable titration method parameters, i.e. a fixed or dynamic titrant increment and a fixed time or equilibrium-controlled signal acquisition:
Mix time: The solution is stirred vigorously (e.g., speed: 70%) and the complex between analyte and titrant is extracted into chloroform.

Separation time: The solution is stirred slowly (e.g. speed 20%) and the two phases can separate. The signal is acquired at the end of the separation time.

The indicator solution consists of a mixture of a **cationic dye** (dimidium bromide) and an **anionic dye** (disulfine blue). The use of this acidic, mixed indicator solution is a further development by Reid et al. [see e.g. ref. 7] of the classical Epton titration.

The color change is monitored in a special two-phase titration beaker by the DP5 Phototrode™ photometric probe at 550 nm.

**Example:** Titration of SDS (anionic surfactant) with Hyamine™1622 as a titrant (cationic surfactant)

1. Before EQP
2. Stirring
3. At EQP
4. After EQP

1. The **anionic surfactant** and the **cationic dye** give a non-polar, *pink-colored* complex which is soluble in chloroform (lower phase) and insoluble in water (upper phase).

2. After each titrant increment, the solution is stirred vigorously and then allowed to separate.

3. During titration, the titrant displaces the cationic dye, and the pink colour slowly disappears from the chloroform phase (lower phase). The dye passes into the aqueous phase.

4. At the EQP, the pink colour disappears, the chloroform phase is colorless and an excess of titrant forms a **non-polar blue complex** with the **anionic dye** in the chloroform phase.

The transmission signal is given in the following figure: At the beginning of the titration, the pink color absorbs all green light (550 nm) of the DP5 Phototrode™. Thus, the signal is only 20-30 mV. When the color has changed to blue, the green light is not absorbed anymore, and a clear jump up to approx. 400 mV is achieved.

![Graph showing the titration process](image-url)
In a similar way, cationic surfactants can be titrated with anionic surfactants using the same mixed indicator solution. In this case, the color change varies from blue to pink, and the curve profile is the opposite of the previous one, i.e. it will start from high transmission value and will decrease to a lower value.

Note that a tested method is stored in the memory of the titrator as application M434.

5.4 Tips and hints
Here are some general Good Titration Practice™ remarks to improve quality of the results:

- Water bubbles can coat the mirror and the window of the DP5 Phototrode™ affecting the signal acquisition. To avoid this, a special two-phase titration beaker (ME-51’107’655) was developed.
- When titrating ionic surfactants, do not choose a too large sample size to avoid foaming during strong stirring.
- Prepare a sample standard solution and titrate aliquots of it.
- Add some mL alcohol to the standard solution to avoid foam.
- High salt concentrations affect the analysis since the formed precipitate can be dissolved again i.e. the color disappears.
- Follow exactly the procedure for the preparation of the mixed acid indicator.
- During titration, the organic solution can also become turbid; it strongly depends on the sample.
- Clean the DP5 Phototrode™ thoroughly after each sample with water or, if necessary, with ethanol.
- When using a sample changer, the introduction of a conditioning step after each sample can improve the cleaning efficacy.
### 5.5 Results of automated colorimetric two-phase titration

<table>
<thead>
<tr>
<th>Anionics</th>
<th>n</th>
<th>Average</th>
<th>s</th>
<th>srel / %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid detergent, M434</td>
<td>6</td>
<td>13.56 %</td>
<td>0.06 %</td>
<td>0.422</td>
<td></td>
</tr>
<tr>
<td>Titer of 0.004 M Hyamine™1622, M606</td>
<td>6</td>
<td>1.0661</td>
<td>0.0224</td>
<td>2.097</td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 1, M607</td>
<td>6</td>
<td>17.84 %</td>
<td>0.612 %</td>
<td>3.43</td>
<td>Fatty alcohol ether, sec. alkanesulfonate, cocamidopropylbetaine</td>
</tr>
<tr>
<td>Conc. liquid detergent 2, M607</td>
<td>5</td>
<td>31.13 %</td>
<td>0.566 %</td>
<td>3.17</td>
<td>Fatty alcohol ether, sec. alkanesulfonate, cocamidopropylbetaine, nonionic surfactants</td>
</tr>
<tr>
<td>Liquid detergent 3, M607</td>
<td>5</td>
<td>33.10 %</td>
<td>0.166 %</td>
<td>0.5</td>
<td>Anionic surfactant A, anionic surfactant B</td>
</tr>
<tr>
<td>Liquid detergent 4, M607</td>
<td>5</td>
<td>13.48 %</td>
<td>0.106 %</td>
<td>0.783</td>
<td>Anionic surfactant as SDS</td>
</tr>
<tr>
<td>Douche gel</td>
<td>5</td>
<td>0.269 mmol/g</td>
<td>0.016 mmol/g</td>
<td>6.070</td>
<td></td>
</tr>
<tr>
<td>Titer of 0.0001 M CPC, M652</td>
<td>6</td>
<td>1.0982</td>
<td>0.0764</td>
<td>6.96</td>
<td></td>
</tr>
<tr>
<td>0.004 M CPC, M652</td>
<td>3</td>
<td>0.9012</td>
<td>0.0043</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>0.001 M Hyamine™1622, M652</td>
<td>4</td>
<td>0.8488</td>
<td>0.0438</td>
<td>5.16</td>
<td></td>
</tr>
<tr>
<td>0.004 M Hyamine™1622, M652</td>
<td>5</td>
<td>1.0078</td>
<td>0.0029</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Drilling emulsion, M652</td>
<td>6</td>
<td>0.1292 mmol/g</td>
<td>0.0006 mmol/g</td>
<td>0.46</td>
<td>Mixture of surfactants: SPS (Sodium petroleum sulfonate), main component is Na-DBS (sodium dodecylbenzenesulfonate)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.1293 mmol/g</td>
<td>0.0015 mmol/g</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.1279 mmol/g</td>
<td>0.0038 mmol/g</td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>Liquid detergent, M413</td>
<td>6</td>
<td>13.88 %</td>
<td>0.04 %</td>
<td>0.275</td>
<td>Anionic surfactant as SDS</td>
</tr>
</tbody>
</table>

n: number of samples  
s: standard deviation  
srel: relative standard deviation (%)  
Mxxx: Application number

For the above table (results from ref. 12) it can be noticed that

1. the surfactant concentration, and  
2. the presence of additional components

can both strongly affect the repeatability of the analysis. In particular, for lower concentrated titrants (see titer determinations) the repeatability, expressed as relative standard deviation, becomes worst and can reach even values of approx. 7%.
6 Potentiometric titrations in aqueous phase

6.1 Principle

The potential of a solution containing surfactants is measured as a function of the added titrant. Potentiometric titrations are indicated with a surfactant sensitive electrode (SSE). Usually, a SSE has a PVC membrane optimized for the detection of ionic surfactants.

The general composition of a typical SSE polymeric membrane is:
- PVC
- Plasticizer
- Ion carrier

The potential is measured in the sample solution with a SSE. Due to the interaction of the analyte with ion carrier molecules (i.e. formation of a complex) in the membrane, a potential is formed at the interface between the solution and the membrane. It can be measured against a reference electrode at zero current. In this way, the potential can be monitored during titration.

Anionic (cationic) surfactants are titrated with cationic (anionic) surfactants. Near the equivalence point, a precipitate is formed, and the solution becomes turbid.

In the case of nonionic surfactants, addition of an aqueous solution of a specific salt, called activator, is necessary prior to titration. The salt cations are complexed by the nonionic surfactant molecules and, in this way, the nonionic surfactant molecules are positively electrical charged. The activator is usually barium chloride, BaCl₂. The positively charged barium cations Ba²⁺ form a complex with the uncharged nonionic surfactant [see ref. 1, 3].

As a result, the surfactant-barium cation complex is positively charged - a pseudocationic complex-. This pseudocationic complex can be precipitated by titration with sodium tetraphenylborate (NaTPB): Tetraphenylborate anions (TPB⁻) form an ion pair with the pseudocationic complex which precipitates in solution.
6.2 Potentiometric SSE titration: Profile of titration curves

The potential-volume E-V curves obtained are usually S-shaped and can be easily evaluated for the largest change in potential. Thus, the standard evaluation is selected in the titration method.

On the right side, the titration curve is shown for the titer determination of Hyamine™ 1622 with SDS. Note the symmetric profile of the titration curve.

On the other hand, if the curve shows a pronounced asymmetric profile, then the asymmetric evaluation can be used. The titration curve illustrated in the figure on the right clearly shows an asymmetric profile.

The curve was obtained by titrating a toothpaste sample with Hyamine™ 1622 to determine the anionic surfactant content [12].

6.3 Practical Hints

Here are some recommendations on the use of a surfactant sensitive electrode for the titration of surfactant in aqueous solution:

- **Caution**: Organic solvents destroy the PVC-membrane!
- A pH value below 2 or above 10 will damage the membrane of the DS500 electrode
- Conditioning of SSEs prior to titration is needed to achieve accurate and reproducible results.
  Examples:
  - Dip the SSE in a standard solution of the surfactant to be titrated.
  - Perform 2-3 trial titrations of the sample to be analysed before starting a series.
- SSEs are only suitable for the titration of low surfactant concentrations in aqueous solutions (10⁻⁴ - 10⁻⁵ mol/L).
- After each sample clean the electrode thoroughly.
- Note that a too high salt concentration can lead to a flat titration curve.
- Appropriate cleaning and conditioning of the electrode after each sample titration are very important to get accurate results.
- Choose the appropriate reference electrolyte to avoid interferences. For instance, replace KCl with 2 M NaNO₃ when using NaTPB for the titration of nonionic surfactants, since the potassium cation K⁺ forms a complex with TPB⁻ anions.
- Conditioning is sometimes also needed for the reference electrode due to diffusion of the sample into the electrode through the ceramic diaphragm. If necessary, replace the electrolyte.
- SSE Membrane module tips do not last forever. Depending on the use and maintenance, they usually have a lifetime between approx. 4-6 months and 1 year.
## 6.4 Results of potentiometric titrations in aqueous phase

<table>
<thead>
<tr>
<th>Anionics</th>
<th>n</th>
<th>Average</th>
<th>s</th>
<th>srel / %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titer of 0.004 M Hyamine™1622, M610</td>
<td>5</td>
<td>0.9967</td>
<td>0.0076</td>
<td>0.761</td>
<td></td>
</tr>
<tr>
<td>Titer of 0.004 M SDS, M611</td>
<td>6</td>
<td>1.0128</td>
<td>0.0046</td>
<td>0.450</td>
<td></td>
</tr>
<tr>
<td>Titer of 0.004 Na-TPB, (AgNO₃ as standard) M612</td>
<td>7</td>
<td>0.91070</td>
<td>0.00610</td>
<td>0.669</td>
<td>Na-TPB: Sodium tetraphenylborate Ref. Electrode: 2 M NaNO₃</td>
</tr>
<tr>
<td>Liquid detergent 1, M613</td>
<td>6</td>
<td>17.27 %</td>
<td>0.110 %</td>
<td>0.639</td>
<td>Fatty alcohol ether, sec. alkanesulfonate, cocamidopropylbetaine</td>
</tr>
<tr>
<td>Concentrated liquid detergent 2, M613</td>
<td>6</td>
<td>34.13 %</td>
<td>0.137 %</td>
<td>0.401</td>
<td>Fatty alcohol ether, sec. alkanesulfonate, cocamidopropylbetaine, nonionic surfactants</td>
</tr>
<tr>
<td>Liquid detergent 3, M613</td>
<td>6</td>
<td>33.85 %</td>
<td>0.416 %</td>
<td>1.23</td>
<td>Anionic surfactant A, anionic surfactant B</td>
</tr>
<tr>
<td>Liquid detergent 4, M613</td>
<td>10</td>
<td>15.25 %</td>
<td>0.145 %</td>
<td>0.951</td>
<td>Anionic surfactant as SDS</td>
</tr>
<tr>
<td>Douche gel</td>
<td>5</td>
<td>0.2684 mmol/g</td>
<td>0.0036 mmol/g</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Recovery of 0.004 M CPC, M613</td>
<td>6</td>
<td>100.62 %</td>
<td>0.73 %</td>
<td>0.728</td>
<td></td>
</tr>
<tr>
<td>Recovery of 0.004 M SDS, M613</td>
<td>6</td>
<td>99.95 %</td>
<td>0.74 %</td>
<td>0.728</td>
<td></td>
</tr>
<tr>
<td>0.01 M SDS</td>
<td>5</td>
<td>100.00 %</td>
<td>0.22 %</td>
<td>0.220</td>
<td></td>
</tr>
<tr>
<td>0.05 M SDS</td>
<td>5</td>
<td>104.00 %</td>
<td>3.68 %</td>
<td>0.728</td>
<td></td>
</tr>
<tr>
<td>Drilling emulsion, M654</td>
<td>6</td>
<td>0.0014 mmol</td>
<td>0.0002 mmol</td>
<td>15.646</td>
<td>Mixture of surfactants:</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.0097 mmol</td>
<td>0.0001 mmol</td>
<td>1.508</td>
<td>SPS (Sodium petroleum sulfonate), main component is Na-DBS (sodium dodecylbenzenesulfonate)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0386 mmol</td>
<td>0.0001 mmol</td>
<td>0.456</td>
<td></td>
</tr>
<tr>
<td>Liquid detergent, M414</td>
<td>6</td>
<td>14.17 %</td>
<td>0.05 %</td>
<td>0.328</td>
<td>Anionic surfactant as SDS</td>
</tr>
</tbody>
</table>

n: number of samples  
s: standard deviation  
srel: relative standard deviation (%)  
Mxxx: Application number (see ref. 12).

From the above table it can be noticed that the surfactant concentration and additional components can both strongly affect the repeatability of the analysis. In particular, for lower concentrated titrants (see titer determinations) the repeatability, expressed as relative standard deviation srel, becomes worse and can even reach values of approx. 15%.
7 Potentiometric two-phase titrations

7.1 Principle

Generally, surfactant sensitive electrodes are exclusively used in aqueous solutions. This is due to the fact that polymeric membranes are damaged when exposed to solutions containing organic solvents such as e.g. chloroform. For example, the DS500 surfactant sensitive electrode can only be used in aqueous surfactant solutions.

As a consequence, it is not possible to benefit from the strong advantage of the presence of a second, organic phase. In fact, when the ion pair complex is formed during titration, this is immediately transferred into the organic phase, whereas other interfering components remain in the aqueous phase. In this way, the quality of the measured potential is improved.

On the other hand, the DS800-TwoPhase is suitable for the indication of anionic and cationic surfactants in two-phase titration according to the standards DIN EN14480, 14668 and 14669 [11]. The electrode is resistant to ketones (methyl isobutylketone MIBK, recommended in the standards), hexane, toluene or ethanol and can be operated in a wide pH range from 1 to 12. The immobilized surfactant-sensitive ionophores in the membrane lead to the formation of a potential at the interface between the membrane and the sample solution. This is due to the complex formation between ionophores and surfactant molecules penetrating into the membrane, similarly to conventional ion selective electrode.

The working principle is based on a titration in a continuously stirred two-phase system consisting of water and MIBK (see below). During titration, an ion-pair complex is formed between the anionic surfactant in the sample (yellow, e.g. SDS) and the cationic surfactant (red, e.g. Hyamine®1622) as the titrant. The complex is extracted into the organic phase (MIBK). When all surfactant molecules have been titrated, a titrant excess leads to a potential jump. The immobilized surfactant-sensitive ionophores in the membrane lead to the formation of a potential at the interface between the membrane and the sample solution. This is due to the formation of a complex between ionophores and surfactant molecules penetrating into the membrane, similarly to conventional ion selective electrodes.
As already mentioned, the DS800 is resistant to MIBK. However, this does not mean that the electrode is resistant to all organic solvents. In fact, the presence of additional organic solvents can lead to a swelling of the membrane, and thus, this will affect the performance of the electrode. For instance, chloroform leads to a strong swelling of the sensitive membrane. Therefore, the use of this electrode is mainly recommended for the titration procedures specified by the DIN EN standards [11].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent swelling (weight gain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBK</td>
<td>48 %</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>600 %</td>
</tr>
<tr>
<td>Hexane</td>
<td>2 %</td>
</tr>
<tr>
<td>Acetone</td>
<td>93 %</td>
</tr>
<tr>
<td>Toluene</td>
<td>48 %</td>
</tr>
<tr>
<td>THF</td>
<td>Dissolution!</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>OK</td>
</tr>
</tbody>
</table>

Solvent behavior of DS800 Sensor Membrane

Raw materials and formulations containing anionic surfactants, soaps in detergents, cleaners as well as quaternary ammonium surfactants can be simply and securely titrated according to the DIN EN standards [11]. The titration curves are similar to the ones obtained in aqueous solutions i.e. the potential-volume curve show a S-shaped profile.

Finally, the potentiometric two-phase titration ensures high quality results with the following advantages:

- Use of environment-friendly, nonpoisonous solvents
- Short titration time and straightforward method parameters
- Can be automated on a Rondo sample changer and Rondolino automated titration stand

7.2 Potentiometric two-phase titration: tips and hints

Here are some recommendations on the use of a surfactant sensitive electrode for the titration of surfactant in aqueous solution:

- The DS800 TwoPhase electrode can not be used in chloroform; the electrode can mainly be used for the MIBK/water two-phase system.
- pH measuring range: pH 1-12.
- Conditioning of SSEs prior to titration is needed to achieve accurate and reproducible results.
  Examples:
  - Dip the SSE in a standard solution of the surfactant to be titrated.
  - Perform 2-3 trial titrations of the sample to be analysed before starting a series.
- SSEs are only suitable for the titration of low surfactant concentrations in aqueous solutions ($10^{-4}$ - $10^{-5}$ mol/L).
- After each sample clean the electrode thoroughly.
• Note that a too high salt concentration can lead to a flat titration curve.
• Appropriate cleaning and conditioning of the electrode after each sample titration are very important to get accurate results.
• The surfactant sensitive membranes do not last forever. Depending on the use and maintenance, they usually have a lifetime of approx. 4-6 months.

7.3 Results of potentiometric two-phase titrations

<table>
<thead>
<tr>
<th>Anionics</th>
<th>n</th>
<th>Average</th>
<th>s</th>
<th>srel / %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titer of 0.004 M Hyamine™1622, M378</td>
<td>5</td>
<td>0.999866</td>
<td>0.001784</td>
<td>0.178</td>
<td></td>
</tr>
<tr>
<td>Shower gel 0214, M376</td>
<td>5</td>
<td>24.667% (pH 3)</td>
<td>0.040%</td>
<td>0.161</td>
<td>Expected: 24%, expressed as SDS</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>24.494% (pH 5.5)</td>
<td>0.033%</td>
<td>0.136</td>
<td></td>
</tr>
<tr>
<td>Shower gel 0273, M376</td>
<td>8</td>
<td>25.290% (pH 3)</td>
<td>0.034%</td>
<td>0.136</td>
<td>Expected: 25%, expressed as SDS</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>25.291% (pH 3)</td>
<td>0.031%</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>Deterg. powder 0411, M376</td>
<td>3</td>
<td>20.274% (pH 3)</td>
<td>0.055%</td>
<td>0.273</td>
<td>Expected: 20%, expressed as SDS</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20.303% (pH 3)</td>
<td>0.073%</td>
<td>0.359</td>
<td></td>
</tr>
<tr>
<td>Formulation 0193 M376</td>
<td>5</td>
<td>9.303% (pH 3)</td>
<td>0.031%</td>
<td>0.332</td>
<td>Expected: 8-9%, expressed as SDS</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.253% (pH 3)</td>
<td>0.048%</td>
<td>0.521</td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 0Liq, M376</td>
<td>6</td>
<td>7.317% (pH 3)</td>
<td>0.060%</td>
<td>0.817</td>
<td>Expected: 5-15%, expressed as SDS</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>7.365% (pH 3)</td>
<td>0.080%</td>
<td>1.092</td>
<td></td>
</tr>
<tr>
<td>Cutting oil 00889-03, M377</td>
<td>6</td>
<td>4.87% (pH 3)</td>
<td>0.03%</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>Cutting oil 01325-01, M377</td>
<td>3</td>
<td>2.73% (pH 3)</td>
<td>0.02%</td>
<td>0.559</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.66% (pH 3)</td>
<td>0.02%</td>
<td>0.734</td>
<td></td>
</tr>
<tr>
<td>Cutting oil 02800-01, M377</td>
<td>6</td>
<td>2.01% (pH3)</td>
<td>0.01%</td>
<td>0.733</td>
<td></td>
</tr>
<tr>
<td>Cutting oil C93 18656, M377</td>
<td>6</td>
<td>61.07% (pH 3)</td>
<td>0.47%</td>
<td>0.764</td>
<td></td>
</tr>
<tr>
<td>Cutting oil V43 18571, M377</td>
<td>6</td>
<td>30.96% (pH 3)</td>
<td>0.08%</td>
<td>0.256</td>
<td></td>
</tr>
<tr>
<td>Cutting oil 11675-01, M377</td>
<td>4</td>
<td>13.57% (pH 11)</td>
<td>0.17%</td>
<td>1.228</td>
<td>0.004 M Hyamine™1622</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>13.61% (pH 11)</td>
<td>0.20%</td>
<td>1.486</td>
<td>0.01 M CPC</td>
</tr>
<tr>
<td>Cutting oil 01125-02, M377</td>
<td>4</td>
<td>4.49% (pH 11)</td>
<td>0.05%</td>
<td>1.155</td>
<td>0.004 M Hyamine™1622</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.55% (pH 11)</td>
<td>0.01%</td>
<td>0.231</td>
<td>0.01 M CPC</td>
</tr>
</tbody>
</table>

n: number of samples  
s: standard deviation  
srel: relative standard deviation (%)  
Mxxx: Application number (from ref. 12, Applications Brochure 35)
The table shows excellent results concerning the accuracy and the repeatability. In particular, the repeatability (expressed as the relative standard deviation) can vary up to 1%, especially at strong alkaline pH values (pH 11). At acidic pH values, i.e. at pH 3 as requested by the DIN EN standards [see ref. 11], the relative standard deviation $s_{rel}$ can achieve very good values in the order of 0.16%.

8 Chemical reactions in surfactant titration

8.1 Anionic/cationic surfactants

For anionic and cationic surfactants, the chemical reaction involved is based on the formation of an ion-pair complex between counter-ionic surfactants. The precipitation of this complex allows for the quantitative determination of the surfactants present in the sample.

For instance, if the content of anionic surfactants has to be determined in liquid detergents, then a cationic surfactant solution such as Hyamine®1622 or CPC has to be used as a titrant. This is the most common example of a surfactant titration.

On the other hand, when cationic surfactants have to be titrated, an anionic titrant such as SDS is used.

The precipitated colloidal complex leads to a turbidity increase and to a potential change. Therefore, such a titration can be indicated using a photometric sensor e.g. DP5 Phototrode™ which monitors the turbidity.

However, if the sample solution is already turbid, then it can not be measured by photometric detection. In this case, a surfactant sensitive sensor (SSE) can be used for the potentiometric indication of the titration, either in aqueous (DS500) or in the MIBK/water two-phase system (DS800 TwoPhase).
8.2 Nonionic surfactants

In the case of nonionic surfactants, an additional sample preparation step has to be performed to achieve a precipitation reaction. In fact, this is due to the fact that nonionic surfactants dissolved into water do not lead to the formation of free ions in solution. Thus, it is not possible to titrate them directly using an ionic surfactant as a titrant.

To precipitate a nonionic surfactant, it is first necessary to charged them electrically by adding metal cations to the solution, i.e. to activate it. The metal cations form a complex with the nonionic surfactants, which is positively charged. For this reason, it is indicated as a “pseudo-cationic” complex.

Generally, almost all nonionic surfactants used in e.g. cosmetic industry contain ethylene oxyde (EO) units in their hydrophobic alkyl chain, i.e. they contain the unit \(-(CH_2-CH_2-O)_n\)-, where \(n\) is the number of such units in a chain. The oxygen oxygen atoms present in the EO-units can complex metal cations such as barium.

By adding a concentrated solution of barium chloride to the sample, nonionic surfactant molecules can complex barium ions leading to the formation of the “pseudo-cationic” complex. As a consequence, this complex can be now precipitated using a bulky counter-ion such as tetraphenylborate, TPB, which is negatively charged.
8.3 Amphoteric surfactants

Betaines (such as cocoamidopropylbetaine) are amphoteric surfactants widely used in the field of cosmetics and cleaning products (washing detergents). The titration of betaines is a challenging task due to the presence of a carboxylic group, R-COO\(^-\), and of a quaternary nitrogen atom, N\(^+\), which is positively charged.

Betaine raw products also contain components which interfere with the titration analysis. The accurate selection of the method is crucial to achieve accurate results.

Here are presented three titration techniques which are mentioned in the scientific literature [see ref. 10] and can be applied for the content determination of betaines:

8.3.1 Precipitation titration with sodium tetraphenylborate

The first method is based on a precipitation titration:

First, the carboxylic group is protonated by addition of acid. To achieve a complete protonation of this group, the pH value has to be adjusted to pH 1. As a consequence, betaine molecules are positively charged. Subsequently, they are precipitated by titration with sodium tetraphenylborate and monitored using a surfactant sensitive electrode.

\[
\text{N}^+\text{-CH}_2\text{COO}^- + \text{B}^- \rightarrow \text{N}^+\text{-CH}_2\text{COO}^- \text{B}^- 
\]

8.3.2 Titration in a non-aqueous solvent with potassium hydroxide

The second technique is based on a titration with potassium hydroxide in a non-aqueous solvent. First, the sample is acidified with a known acid excess to protonate the carboxylic group, and then the sample is titrated.

\[
\text{N}^+\text{-CH}_2\text{COO}^- + \text{KOH} \rightarrow \text{N}^+\text{-CH}_2\text{COO}^- \text{K}^+ 
\]

8.3.3 Titration in a non-aqueous solvent with perchloric acid

In the third method, the pH of the sample is adjusted with a pH buffer, and then titrated with perchloric acid in a non-aqueous solvent.

\[
\text{N}^+\text{-CH}_2\text{COO}^- + \text{HClO}_4 \rightarrow \text{N}^+\text{-CH}_2\text{COO}^- \text{HClO}_4^- 
\]

Generally, these techniques are applied in raw products of known composition. Betaine samples of unknown composition can be determined only by suitable combinations of these methods.
9 Surfactant titration: Comparison of different techniques

9.1 Titer determinations with standard solutions

A useful test of the different methods is the titer determination using the same standard solution (SDS and CPC, respectively). A comparison of the results is shown in table 1 (see ref. 12, Brochure 22). The precision (repeatability), indicated by the relative standard deviation srel, is very good for all methods, with values reaching down to 0.183 %.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Automated Colorimetric 2-Phase</th>
<th>Turbidimetric</th>
<th>Potentiometric SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Titer</td>
<td>srel (%)</td>
</tr>
<tr>
<td>Hyamine®1622</td>
<td>5</td>
<td>1.0461</td>
<td>0.562</td>
</tr>
<tr>
<td>SDS</td>
<td>3</td>
<td>0.9560</td>
<td>0.821</td>
</tr>
</tbody>
</table>

The titer values vary from 0.9967 to 1.0461 for Hyamine®1622, and from 0.9560 to 1.0319 for SDS. The 2P-titration method gives slightly different titer values (1.0461 for Hyamine, and 0.9560 for SDS) than with the turbidimetric and potentiometric techniques. This is mostly due to the formation of water bubbles in the lower organic phase –trapped in the measuring cell of the DP5 Phototrode™-, and of an emulsion leading to an increase the turbidity. This affects the photometric detection with the DP5 Phototrode™.

9.2 Recovery tests with SDS and CPC solutions

5 mL 0.004 M SDS and 0.004 M CPC have been used as standard solutions to test the recovery. The samples were titrated with 0.004 M Hyamine®1622 and SDS, respectively. The results have been summarized in table 2 (see ref. 12, Brochure 22).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Automated Colorimetric 2-Phase</th>
<th>Turbidimetric</th>
<th>Potentiometric SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Recovery (%)</td>
<td>srel (%)</td>
</tr>
<tr>
<td>SDS</td>
<td>4</td>
<td>98.28</td>
<td>1.78</td>
</tr>
<tr>
<td>CPC</td>
<td>4</td>
<td>100.86</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Very good agreement with the theoretical value of 100% was achieved with all methods and both standard solutions of SDS and CPC, although the precision of the automated colorimetric two-phase titration was only ca. 1.8 %. This is mainly due to the formation of small water bubbles on the mirror and window of the DP5 Phototrode™ screw-on assembly during signal acquisition (slow stirring speed). The small water bubbles lead to a noisy signal. As a consequence, a lower repeatability is achieved, as indicated by the higher srel values.
9.3 Anionic content determination in formulated products

Two formulations (Liquid det. 1 and 2) and two commercially available products (Liquid detergents 3 and 4) have been analysed by different methods. Where possible, composition, type and content values of the surfactants were indicated (information from the producer).

To allow a significant comparison, the pH value of the aqueous sample solution was adjusted to pH 1-2 by adding 10 mL 0.1 M sulfuric acid. In this way, the same pH value conditions as for the classical colorimetric two-phase titration have been reproduced. Otherwise, the indications in the analysis procedure given by the producers have been followed (Liquid detergents 1 and 2 have been analysed at pH 3 in order to take into account for the betaine content).

Note that the determinations with a surfactant sensitive electrode (SSE) in aqueous solutions were all performed at pH 3 since a pH lower than 2 can damage the sensitive membrane of the surfactant electrode.

Table 3: Anionic content determinations in various samples (from ref. 12, Brochure 22)

<table>
<thead>
<tr>
<th></th>
<th>2P Content (%)</th>
<th>DP5 Content (%)</th>
<th>SSE Content (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>srel (%), (n)</td>
<td>srel (%), (n)</td>
<td>srel (%), (n)</td>
<td></td>
</tr>
<tr>
<td>Liq. det. 1 Average M=387</td>
<td>17.84 (3.43 (6))</td>
<td>17.24 (0.09 (5))</td>
<td>17.27 (0.64 (6))</td>
<td>17.1 pH3 (Reference) (%) 18.0 Fatty alcohol ethersulfate 10% Secondary alkanesulfonate 6% Betaine 2%</td>
</tr>
<tr>
<td>Liq. det. 2 Average M=362</td>
<td>31.13 (3.17 (5))</td>
<td>34.49 (-0.02 (5))</td>
<td>34.13 (0.40 (6))</td>
<td>32.8 pH3 (Reference) (%) 38.5 Fatty alcohol ethersulfate 11% Secondary alkanesulfonate 20% Betaine 3.5% 7 EO Nonionic 4%</td>
</tr>
<tr>
<td>Liq. det. 3 Average M=359.09</td>
<td>33.10 (0.50 (5))</td>
<td>30.94 (1.97 (7))</td>
<td>34.58 (0.28 (6))</td>
<td>- pH1-2 (Reference) (%) 33.0 Anionics A (M=346) 27% Anionics B (M=385) 6% additional comp. unknown</td>
</tr>
<tr>
<td>Liq. det. 4 As SDS Average M=288.38</td>
<td>13.48 (0.78 (5))</td>
<td>13.24 (0.94 (4))</td>
<td>16.35 (0.28 (6))</td>
<td>14.18 pH1-2 (Reference) (%) 15-30% Anionic surfactants unknown composition</td>
</tr>
</tbody>
</table>

Nominal value: Theoretical composition of the sample as total washing active matter. It is obtained by summing the percentages of all surfactant components in the sample.

Reference: Value given by the producer and mostly based on classical two-phase titration. It indicates the total washing active matter.

(n): Sample number

srel: Relative standard deviation (%)

(-): Sample dissolved in water without pH adjustment.
**Liquid detergent 1:**
This product contains 10% fatty alcohol ethersulphate, 6% secondary alkanesulphonate, and 2% betaine (nominal value: 18% washing active matter, average M = 387 g/mol). According to the producer, 2P-titration is performed at pH 3 (average content result: 17.1%) to avoid interferences due to betaines [4].

This is shown by the results obtained with the standard acid mixed indicator (pH 1-2). At this pH value, betaines are mainly protonated and they precipitate other anionic surfactants present in the sample. Thus, these precipitated anionic surfactants are not available anymore for the titrant. As a consequence, the anionics content is lowered, as indicated by the results giving lower content value by approx. 3.3%.

On the other hand, all results obtained at pH 3 agree very well with the reference value, and their values vary from 17.05% to 17.84%. This clearly indicates that the betaines are not interfering with the determination of the anionic surfactant content.

**Liquid detergent 2**
Liquid detergent 2 has a similar composition in comparison to the previous sample. Additionally, nonionic surfactants are contained in the formulated product (average M = 362 g/mol). As indicated by the producer, a 2P-titration performed at pH 3 gives a reference value of 32.8% (average M = 362). Measurements at pH 3 vary between 31.13% and 35.30%. Note the low precision achieved with the automatic 2P-titration (srel: 3.17%) relative to the other techniques, i.e. turbidimetric and potentiometric surfactant titrations.

Particularly low are the content values obtained at pH 1-2, i.e. ca. 30.5 %, although the repeatability is very good (down to srel: 0.10%). This is to be expected since at this pH value betaines are protonated and neutralize other anionic surfactants, and therefore the latter can not be precipitated by titration.

For all techniques, the comparison of content values obtained at pH 3 and without pH adjustment confirms this explanation. Moreover, the large content of secondary alkanesulphonate (20%) may be a conceivable reason for the higher values found by potentiometric titration with a SSE both at pH 3 and without pH adjustment.

**Liquid detergent 3**
The anionic content has a nominal value of 33%, which consists of 27% of surfactant A (M=346) and 6% of component B (M=385). Nature and chemical structure of these surfactants are unknown. Based on this information, an average molecular weight of M=353.09 was calculated.

The results obtained at pH 1-2 with automated, colorimetric two-phase titration and potentiometric (pH 3) techniques are in good agreement with the nominal value of 33% (absolute deviations: 1-2%). However, the turbidimetric method shows a considerably lower content, although the precision is excellent (srel down to 0.07%). Since the composition is not known in detail, it is only possible to speculate on such a low content value. For instance, the protonation of betaines at pH 1-2 may be a reason for an uncomplete precipitation, since protonated betaines precipitate anionic surfactants.

This is also suggested by the results obtained without pH adjustment, i.e. when the sample is simply dissolved in water. In this case, a higher content of 34.44% is found. This value indicates the presence of surfactant species strongly dependent on pH value, as e.g. betaines.

Furthermore, this hypothesis is confirmed by potentiometric determinations with SSE at both pH 3 and without pH adjustment. The results are slightly higher (34.58% and 33.85%,...
respectively) than the nominal value of 33%, and the precision varies between 0.28% (pH 3) and 1.23% (without pH adjustment).

**Liquid detergent 4**
The only information available on the composition of this product was the indication of an anionic surfactant content of 15-30%. Thus, to able to compare the results obtained with the different titration techniques, the content was expressed as % SDS (M=288.38). An independent laboratory performed the determination by mixed classical 2P-titration, achieving a value of 14.18% (SDS). This value was set as a reference for the comparison.

The content values obtained with the different techniques show a good agreement with the reference value of 14.18%, with an absolute content deviation ranging from 0.94% to 2.17%. Again, potentiometric titration at pH 3 shows a slightly higher content of 16.35% at pH 3 with respect to the other techniques. Since the composition is unknown, the exact reason for this slightly higher value can hardly be defined. Thus, conceivable explanations may be:

1) The higher sensitivity of the SSE with respect to photometric techniques [4],

2) If present, betaines can affect the anionic content determination at pH 1-2,

3) 2P-titration: incomplete precipitation and extraction into the chloroform phase.

Since the composition is unknown, the effect due to additional components can not be quantified exactly.
10 Conclusions

There is no general titration method which can be used for all possible formulations and products. When the sample consists of one pure surfactant component, e.g. in raw materials, the determination is straightforward.

In the case of formulations, i.e. products containing various surfactants and additional components, a specific method with appropriate detection technique must be chosen, developed and optimized taking into account:

- Additional surfactant components present in the sample;
- Appropriate pH values;
- Additional components such as salts, abrasive particles, fragrances.

10.1 Automated colorimetric two-phase titration (2P):

Despite the use of chloroform, this technique is still the reference method for surfactant titration in a large number of samples. Its main advantage is the extraction of the non polar titrant-analyte complex into the organic phase: matrix effects, i.e. interferences due to presence of additional components, can be avoided. The colorimetric 2P-titration can be automated by a dedicated titration method function and a photometric sensor such as the DP5 Phototrode™. This method is particularly suited for the analysis of anionic and cationic surfactants. Methods based on 2P-titration of nonionic surfactants containing EO-units and of amphoteric surfactants are also described in the literature [in particular, see ref. 1 and 3].

10.2 Turbidimetric titration:

A fast method is the turbidimetric titration of ionic surfactants with photometric indication. The DP5 Phototrode™ does not need a specific conditioning, and the maintenance is reduced to the minimum. Also the use of organic solvents is avoided. On the other hand, there is no extraction of the complex into the organic phase, thus interferences can become relevant.

This method is most suited for ionic surfactants. In addition, nonionic surfactants (raw materials) and pure solution of betaines (amphoteric surfactants) can be titrated using sodium tetraphenylborate as a titrant.

10.3 Potentiometric techniques: SSE and nonaqueous titration

The titration of ionic surfactants by a surfactant sensitive titration (SSE) in aqueous and in a mixed two-phase system is rather straightforward. These sensors are suitable for the analysis of all types of surfactants, but appropriate conditioning and accurate maintenance of the SSE become very relevant. Thorough cleaning of the SSE membrane is crucial, since it can be coated by the precipitate.

On the other hand, the potentiometric two-phase titration of surfactants represents a considerable development in this field since the advantage of the extraction into the organic phase is combined with the ease-of-use of a potentiometric technique.

Note that a surfactant sensitive electrode can only be used for the indication of a titration, and not for the direct measurement of surfactant concentration in aqueous solution due to the formation of micelles by surfactants molecules in solution.

Finally, the acid/base potentiometric titration in nonaqueous solution using a pH-combination electrode has to be mentioned for the determination of betaines, the most used amphoteric surfactants in cosmetics. With this method, the content of betaines can be determined in e.g. a shampoo.
11 Literature


[12] «Surfactant titration»

«Selected METTLER TOLEDO Methods for Titration Excellence Line»
Mettler-Toledo Titration Applications Brochure No. 34, ME-51725066A, November 2006.

«Selected Applications for METTLER TOLEDO Titration Excellence Line»
Mettler-Toledo Titration Applications Brochure No. 35, March 2008 (PDF file only).

General literature:


Literature on kinetics of surfactant titration (precipitation):

This application bulletin represents selected, possible application examples. These have been tested with all possible care in our lab with the analytical instrument mentioned in the bulletin. The experiments were conducted and the resulting data evaluated based on our current state of knowledge.

However, the application bulletin does not absolve you from personally testing its suitability for your intended methods, instruments and purposes. As the use and transfer of an application example are beyond our control, we cannot accept responsibility therefore.

When chemicals and solvents are used, the general safety rules and the directions of the producer must be observed.
Good Titration Practice in Surfactant Titration

Good Titration Practice™ (GTP) in general encompasses three important steps:

1. **Evaluation**
   of the appropriate titration system (DQ) i.e. evaluation, specification of the analytical requirements and purchase decision.

2. **Installation**
   of the selected analytical system comprising IQ and OQ and training of personnel.

3. **Routine**
   operation including PQ, method validation, development of SOPs and maintenance of the validated state of the analytical system.

This brochure specifically focuses on Good Titration Practice in surfactant content determination. It outlines specific aspects in developing and maintaining a good routine operation with METTLER TOLEDO Titration Excellence Instruments as well as dedicated sensors and accessories for surfactant titration.

The GTP Surfactant Titration Brochure and the Application Brochure 22 containing dedicated applications on various samples, are two powerful tools which are meant to facilitate your content determination analyses and to contribute to reliable results over the whole lifetime of your instrument.